8-1-1991

An Investigation of the potential mobility of gold ions in core/shell silver bromide emulsions

Thomas Scarsella

AN INVESTIGATION OF THE POTENTIAL MOBILITY OF GOLD IONS IN CORE/SHELL SILVER BROMIDE EMULSIONS

by

Thomas M. Scarsella

B.S. SUNY Brockport

(1980)

A thesis submitted to the
Center for Imaging Science at the
Rochester Institute of Technology
as part of the requirements for the
completion of the degree Master's of Science

August 1991

Signature of the Author_____

Accepted by Mehdi Vaez-Iravani
Coordinator, M.S. Degree Program

COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY
ROCHESTER INSTITUTE OF TECHNOLOGY
ROCHESTER, NEW YORK

CERTIFICATE OF APPROVAL

M.S. DEGREE THESIS

The M.S. Degree Thesis of Thomas M. Scarsella has been examined and approved by the thesis committee as satisfactory for the thesis requirement for the Master of Science degree

Prof. Harry E. Roberts, Thesis Advisor

Dr. Judith M. Harbison Committee Member

Prof. Richard K. Hailstone, Committee Member

January 6, 1992
Date

THESIS RELEASE PERMISSION
ROCHESTER INSTITUTE OF TECHNOLOGY
COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY

For the thesis entitled An Investigation of the Potential Mobility of Gold Ions in Core/Shell Silver Bromide Emulsions, I Thomas M. Scarsella hereby grant permission to the Wallace Memorial Library of the Rochester Institute of Technology to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

Date: February 7, 1992

ABSTRACT

The degree to which non-localized gold ions migrate to the surface from the core of a silver bromide core/shell octahedral emulsion in the absence of sulfur sensitization is investigated. An octahedral core emulsion is precipitated in an oxidized gelatin environment, sensitized with gold, and covered with an additional layer of silver bromide. It was postulated that the migration of gold might be detected by a significant increase in the surface speed of the emulsion due to the catalytic enhancement of latent image formation typified by gold, and an increase in the tendency of the system to form developable sites on the grain surfaces upon application of a solution of stannous chloride. The results were less than conclusive.

The author wishes to acknowledge those people without whom this thesis could never have been completed. Special thanks go to Professor Elvin Thurston for his insight, willingness to share his many years of experience in the field, and for overseeing much of the day to day work. I would like to thank both Prof. Roberts and Dr. Harbison for their knowledge and patience. My most heartfelt appreciation goes to those of the faculty, staff, and students of the Center for Imaging Science that I number among my friends. Without your companionship and encouragement I would not have persevered.

This thesis is dedicated to the memory of my father, Arthur and to that of Ronald Francis. Their confidence in me was unwaivering; each always made time for me despite the heavy burdens they had to bear. I am fortunate to have known them both. If I live up to their high standards and expectations I will have done well.

Table of Contents

List of Figures

List of Tables

1.0 INTRODUCTION

Previous work on the mechanisms by which gold contributes to the quantum efficiency and stabilization of latent image formation has not adequately addressed the role of internal gold sensitization in the absence of sulfur sensitization (Mueller, 1966, Faelens, 1978). The well known synergism between sulfur and gold (James, 1948, Harbison, 1975, Farnell, 1976, 1980, Cash, 1983) has not encouraged inquiry into the role played by gold alone in silver halide materials where gold ions are not tied to specific sites within the crystal lattice.

Sulfur-plus-gold sensitization is explained as an interaction between two different mechanisms (Moisar, 1981), one associated with each ionic species. It is thought that the incorporation of anions of similar size and greater charge than bromide in silver halide crystals cause immobile defects in the lattices (Sayhun, 1982) which enhance their primitive sensitivities (Hamilton, 1983) and function as centers for latent image nucleation and growth.

Sulfur sensitization is carried out by ripening an

emulsion in the presence of compounds possessing labile sulfide (Pitt, 1981). This ripening may be carried out on an emulsion once the silver bromide crystals have been grown to a fraction of their final diameter. In this case sulfur sensitization sites, which had been formed on the surface on the crystals, are covered over and made internal by precipitating additional silver bromide over the entire grain. In this way control is exercised over the depth of the sulfur sensitization sites within the emulsion grains (Evans, 1973).

The greater negative charge of sulfide, when occupying lattice sites typified by bromide ions (Galvin, 1972), results in associated local charge imbalances. The accompanying physical defect is due to the deformation undergone by the lattice as its constituent ions and their electron shells are shifted to incorporate the more highly charged sulfide ion and its electron shell. This distortion is not due solely to the size difference between the sulfide ion and the bromide which it is replacing. The size difference between the two species of ions is quite small. The defect is caused by nearby bromide ions being repelled by the negative charge possessed by the sulfide which also exerts a strong attractive force on any nearby

silver ions, pulling them inwards.

Positively charged interstitial ions can reduce or eliminate local charge imbalances within the lattice. Mobile cationic impurities of sizes appropriate for interstitial migration through face centered cubic lattices such as silver halide are attracted to the defect sites which result from the incorporation of ions such as sulfide which have charges other than minus one. The presence of cationic gold in interstitial sites in the vicinity of a sulfide ion may also reduce the local distortions in charge associated with an incorporated divalent anion.

In the absence of other doping agents, any cations attracted to a sulfur (Kellogg, 1975) defect during exposure by the currently accepted alternating-growth model (Hamilton, 1982) for latent image nucleation and growth would be silver ions alone (Moisar, 1977). When gold ions are present as additional sensitizing agents, they may migrate as interstitials through the crystal lattice with greater freedom than do silver ions. The theorized high mobility of interstitial gold ions might be due to the increased diffusion energy (Deri, 1985) caused by their smaller numbers as compared to those of

interstitial silver ions.

Previous work has indicated that ionic gold within the silver halide lattice possesses an enthalpy lower than that of interstitial silver ions (James, 1948). The lower amount of energy required to move gold between neighboring interstitial sites as compared to the energy required to move interstitial silver ions accounts for the disproportionate amount of time gold is found in the vicinity of lattice discontinuities such as those described above (Tan, 1981).

It can therefore be stated that an individual ion of gold has a much greater chance of diffusing to a charged defect site of the type likely to result from a lattice defect than does a particular ion of free silver. Once diffused to such a defect a gold ion may be trapped in preference to an ion of silver due to differences in the energy levels possessed by the ions involved. The lower limit of the energy band characteristic of gold is below that of silver. A mixed ion pair results in the formation of high and low levels intermediate of the two species.

This is explained by the greater difference in the

energy levels (Mueller, 1966) of a gold-silver ion pair as compared with those of a silver-silver ion pair (Locker, 1976). The low energy level of a silver-gold ion pair favors the trapping of a gold ion in either an empty or partially filled trap site over an interstitial silver ion. This relationship holds true even at low pAg's where the interstitial silver ions exist in numbers far greater than gold. Gold, once diffused to a defect site increases the formation efficiency of latent images as compared to those defect sites containing silver ions alone (Spencer, 1987). The catalytic development of latent images containing both silver and gold is greater than that for those containing silver only (James, 1948).

Overall sensitivity to light in that part of the spectrum where silver halide exhibits 'primitive' sensitivity may increase significantly when gold is present and localized (James, 1977). This is a measure of photographic speed as determined by:

$$\text{speed} = \frac{0.8 + B + F}{\text{Log } H}$$

Where B is the measured density of the film support and subbing layers, F is the density of the fog in the

unexposed portions of the developed film, and Log H is the exposure imparted to the film sample expressed as the logarithm of meter candles.

Gold incorporated into an emulsion in the absence of a localizing agent has a different effect on photographic sensitivity. The formation and development of latent images on the surface of the silver halide grains (Tani, 1983) may show some enhancement (Burge, 1982), but the loss of internal speed that results from gold not being localized at the sensitivity center at the time of exposure exceeds any improvement (Harbison, 1975). The localization of the gold ions at the crystal surface (Sutherns, 1961), which behaves as a negatively charged defect because of space-charge considerations, is possibly due to the lack of competing defects within the body of the silver halide grains (Marchetti, 1984).

In the absence of sulfur or similar anionic dopants, unreduced gold ions should be free to migrate within a silver halide crystal as do silver ions rather than concentrating in zones around defect sites (Junkers, 1974). Since the effective surface charge on a silver halide lattice is negative, gold should be attracted to the surface of silver halide and concentrate in a zone

a short distance (Sturmer, 1975b) below the surface.

An aspect of gold sensitization which has not been fully addressed is the manner in which gold in such a subsurface zone (Hailstone, 1987) interacts with other types of sensitization in the absence of sulfur. The most interesting possibility being the interaction of gold with reduction sensitization (Codling, 1975). Reduction being the third type of chemical sensitization most commonly used after sulfur (Spencer, 1968) and sulfur plus gold.

Reduction sensitization differs from the other two principal types of chemical sensitization in that it is only rarely used by itself. It is commonly used as an additional chemical sensitization after sulfur for print films prone to low intensity reciprocity failure (Collier, 1982). Reduction differs substantially from other types of chemical sensitization by the high instability of the silver metal atoms formed by successful reduction. The stability of the hole traps and sub-latent image specks formed by reduction sensitization can be improved by the addition of a gold ion to a reduction center (Babcock, 1975).

The silver metal specks deposited on the surface of silver halide grains by the successful application of a reducing agent are of two varieties (Collier, 1976, Hamilton, 1981). The two species have different functions, both contributing to an increased efficiency in the mechanism of latent image formation (Collier, 1979) associated with reduction by decreasing the number of photons (Babcock, 1976) which need to be captured for latent images to build (Tani, 1971a) to a stable and developable size (Tani, 1974). The two types of reduction centers which can be formed are site-specific (Tani, 1971b) to different surfaces characteristic of silver halides (Tani, 1972).

If a reduction center forms at a positively charged site it is capable of capturing electrons and growing to latent image size by the accepted alternating growth mechanism previously proposed (Hamilton, 1982). In this model the dominant role of the reduction center is played by those specks which form at electrically neutral sites typical of {100} surfaces and are therefore incapable of trapping electrons and silver ions in alternation. These specks do not grow to latent image size but function as traps for positive holes (Tani, 1974) thereby decreasing speed loss due to

the recombination of free holes and trapped electrons. Such potential sites do not exist on the {111} surfaces which bound octahedral grains. Octahedra do possess large numbers of crystal defects which are believed to diminish the losses inherent to latent image formation from recombination (Tani 1971b).

This investigation is concerned with the potential mobility of gold ions as interstitial species in a core/shell emulsion in the absence of sulfur. Secondary topics of concern include the effects of oxidation on the formation of gold-gelatin complexes, and the effectiveness of the core/shell interface as a source of lattice defects which may localize gold. By these experiments I hope to have added to what is known about gold migration in sulfur-free core/shell emulsions and provide evidence of the presence of gold in fog formed by reduction sensitization.

2.0 Experimental

The investigation required that a monodispersed octahedral emulsion that was half the mean diameter of the finished emulsion be precipitated for use as cores for the core/shell grains that were to be grown. One of the physical constraints considered in the determination of the grain size was the limitation on maximum grain size which could be produced within the silver halide laboratories in the Center for Imaging Science with only two precipitation procedures. A large grain size is preferable as this insures a thick coverage of the core of the final emulsion. The experimental design called for a final diameter of 0.32 microns. The mean diameter of the cores was 0.16 microns which is half the diameter of the finished grains.

One set of precipitation conditions for the octahedral cores was generated by computer simulation (Zuleta, 1987). This would have required a precipitation time of 49 minutes at 55 degrees Celsius with 0.66 Molar solutions of silver nitrate and potassium bromide pumping at 2.50 and 2.54 milliliters per minute, respectively. The required pAg for

nucleation would be 7.5; after two minutes the pAg would be adjusted to 8.94 by the dropwise addition of a solution of potassium bromide. These potentials are directly measured by monitoring the voltage potential of the emulsion kettle during precipitation. The desired pAg is translated into a voltage potential by means of the formula:

$$VAg=602-0.1(T-298)-0.1984(T)pAg$$

Where VAg is measured in absolute millivolts, T is the temperature in degrees Kelvin of the system, and pAg is the potential for silver ion required for the system to yield the correct grain morphology. A short routine for use with programmable calculators was written to facilitate the rapid assessment of conditions during the emulsion making stages of the experiment (Appendix A). Control limits were plus or minus five millivolts from the target values. The recommended limits for nucleation under these conditions would be 106.0 to 111.0 millivolts for nucleation and 12.0 to 22.0 millivolts for the growth stage which commenced two minutes into the precipitation routine. The predicted mean diameter of the cores under these conditions was 0.16 microns.

Empirical methods were used to determine at what point during simple ramped addition routines of known result the desired mean core diameter was reached as shown in Figure 1 (Appendix B). These methods were supported by the results obtained by previous workers within these laboratories. Some of the more recent work has been predicated on the use of low solution concentrations and large vessel volume. This technique permits the nucleation of comparatively few crystals and allows them to be grown to large size under less variable conditions than would be possible with extended growth periods. Nucleations carried out with 0.66 Molar solutions of both $AgNO_3$ and KBr run in at an initial rate of 2.5 mL/minute for 2 minutes at a pAg of 7.5 produced relatively few seeds. After the nucleation stage, pAg was adjusted with the dropwise addition of a solution of potassium bromide to 8.5 and the flow rates were increased to approximately 12.5 mL/minute for each over a 10 minute period. This was continued until one mole of each solution had been run in. Micrographs indicated octahedra with average edge lengths of 0.33 microns and diameters of 0.466 microns (Whitenack, 1988).

By knowing the finished grain size and the amount of

material run in it is possible to extrapolate that a mean crystal diameter of 0.16 microns was reached 7:45 into the ramped flow. This is 9:45 after the precipitation was begun.

The finish size required for the present work would be reached after 444 mL of 0.66 Molar silver nitrate and 451 mL of 0.66 Molar potassium bromide had been delivered to the emulsion kettle. This volume is reached after a cumulative running time of 41:05. These figures were the basis for the ramped flow routines employed for the thesis. (Appendix C).

The nucleation and growth stages of the experiments were carried out in oxidized gelatins that were prepared by adding 85 micromoles of hydrogen peroxide per gram of gelatin to a 12% gelatin solution at 40 degrees Celsius and a pH of 5.6 and allowing it to stand for 16 hours (Maskasky, 1987).

The core emulsion was precipitated into 750 mL of distilled water at 65 degrees Celsius in which 46.88 grams of oxidized phthalated gelatin had been dissolved. This was done at a pH of 2.0 to avoid the trace reduction sensitization (Collier, 1982) that can

occur in the lower ranges of pAg. The pH of this precipitation was sufficiently low that some problems with the subsequent coagulation washing of the cores were encountered. By precipitating the cores in a gelatin solution of a concentration far in excess of the minimal one percent solution commonly used difficulties with the coagulation washing were minimized.

Twice the quantity of cores required for each stage of the thesis were grown to allow for errors in subsequent procedures and normal losses. The cores were taken from the same kettle for each treatment combination in a given design. The volumes of the silver and bromide solutions run into the kettles were larger than required to enhance control over the system. The bromide to silver ratio was set at 1.016 and maintained during all nucleation and growth stages to reduce the likelihood of unwanted renucleation. Portions of the core emulsion were grown to final size by the renewal of the ramped flow routine. The flow rates were adjusted downwards to a lower point on the ramp scheme where the flow rates were in harmony with the reduced surface area of the smaller sample. The program conditions are shown in Figure 2 (Appendix D).

This reduction in flow was necessary to avoid the renucleation which would have resulted from additional silver halide material being added to the kettle at a rate beyond that which could be incorporated onto the surfaces of the existing grains (Appendix E).

The .16 micron cores that were grown from the seeds comprised one eighth of the total volume of the finished grains. This ratio is not atypical for core/shell emulsions described in the literature.

Following the precipitation of the cores the pH of the kettle was adjusted to 2.82, the empirically determined isoelectric point of the oxidized phthalated gelatin for coagulation washing. This eliminated the need for a salt laking procedure (Hewitson, 1952) which was the backup procedure for coagulating these emulsions had they shown no signs of settling by means typically employed by the experimenter.

The supernatant liquor was decanted off and the pH of the emulsion was raised to 4.5 by the dropwise addition of a solution of sodium hydroxide for redispersion. This was followed by a second coagulation

and decanting. This procedure removed by-product salts formed during precipitation by the nitrate ligands and potassium and unwanted compounds added to the emulsion in earlier steps.

After washing the core emulsion was divided and half was reserved. The remainder was used to grow different core/shell combinations required by the experimental design. The division scheme is shown in Figure 3 (Appendix F).

A fraction of the cores was used to grow shelled grains undoped with gold. These served as the control for the experiment. The remainder of the cores were sensitized with two different levels of potassium tetrachloroaurate. One half of each of these combinations was also reserved in the initial experimental run for later work as required. Portions of the remainder were covered over with additional silver bromide to a thickness of .32 microns during the shelling process.

Covering a portion of the cores to final shell thickness required the addition of eight times as much silver halide as was present in the core emulsion to be

covered. Shelling was carried out by continuing with a ramped flow, in which rates were adjusted to a point in the routine where the surface area of the emulsion in question was great enough to take up the new material without renucleation occurring.

The differentiation between the high and low gold combinations was initiated at the completion of core growth. The low gold fractions were sensitized at a level equivalent to 3.2 milligrams of gold per mole of .16 micron octahedra. The high gold fractions were sensitized with four times this amount. The working maxim being that increasing the volume of the average grain eight times would increase their surface area only four times. The required math is included in the Thesis (Appendix G).

Gold sensitization at crystal surfaces was carried out with potassium tetrachloroaurate for 30 minutes at 55 degrees Celsius at the levels described. The emulsions were then washed using coagulation and redispersal at their isoelectric points as had been done for the unsensitized cores. The supernatant fluids are believed to have carried away much of the addenda and any gold not incorporated into the cores.

The cores were subsequently shelled using a ramped flow identical to that employed on the gold free cores. The emulsions were washed again by coagulation and redispersal as previously described subsequent to their being shelled to a total thickness of .32 microns.

Reduction sensitization of each treatment combination was the last step of emulsion preparation. Samples of each emulsion were sensitized at 55 degrees Celsius with an amount of stannous chloride equivalent to 0.5 milligrams per mole of silver bromide over a 30 minute period. The stannous chloride solution was freshly prepared from a dedicated container and was dissolved in a dilute solution of hydrochloric acid to increase its stability.

The level of reduction sensitization employed was equal to that employed by Collier (Collier, 1982) when the higher surface area per mole of material in these emulsions, typified by smaller crystals, was considered. Any residual oxidizer within the gelatin which was not removed during any of the preceding washes may have to some degree hindered the effectiveness of the reduction to a degree which would

be equal in all cases.

The experimental design is outlined in Table 1.

Table 1
Experimental Design

TREATMENT COMBINATION	R	g	G
(1)	-	-	-
a	+	-	-
b	-	+	-
ab	+	+	-
c	-	-	+
ac	+	-	+

Key to Table 1:

(1) is the unsensitized control sample.

R : Emulsion is reduction sensitized with 0.5 mg of stannous chloride per mole of silver after the emulsion has been grown to final size.

g : Core is gold sensitized with 0.8 mg of potassium tetrachoroaurate per mole of silver before the addition of the shell.

G : Core is gold sensitized with 3.2 mg of potassium tetrachoroaurate per mole of silver before the addition of the shell.

The addition of sodium nitrite is one possible method for neutralizing excess oxidizer within the kettle that might have been employed had reduction been

found to be not occurring where it was expected.

The target silver coverage for coating was 100 milligrams of silver per square foot of coated film base which is equal to 108 micrograms per square centimeter. This concentration of silver is equal to an overall molarity of silver of .086 for the solution to be coated. To achieve this concentration of silver within a sample to be coated the emulsions were prepared at a higher concentration of silver which, when diluted with the necessary addenda, would result in the finished emulsion having the correct coating weight.

A typical coating run would call for 10.5 milliliters of an emulsion containing 0.255 Moles of silver per liter and 14.5 milliliters of a solution of twelve percent oxidized inert gelatin to coat a web of 275 inches square.

Addenda were added to each 25 milliliter sample prior to its being coated. The principal addenda added to each sample was 0.8mL of 7% saponin, a wetting agent which improved the flow characteristics of the gelatin for coating purposes. The emulsions were prehardened

prior to their being coated by the addition of 0.2 mL of 40% formaldehyde to each 25mL sample. Use of a hardening agent such as formaldehyde was desirable to shorten the set time required for each coating prior to its removal to a drying cabinet to free up the coating apparatus for another run. The use of a hardener also results in a more durable coating.

The experimental emulsion combinations were coated on a Polaroid loop coater which laid down 25 mL of prepared emulsion on a path five inches wide and fifty-five inches long on pre-subbed five and a half inch wide film base.

The web drive was set to move the film base at a rate of 6.75 feet per minute past the coating head. The emulsions were extruded through a .005 inch gap in the coating head at a temperature of forty degrees Celsius. The emulsions were delivered to the coating head by a Harvard Drive syringe which forced the emulsion from the coating head at a rate of 15.3 milliliters per minute. After being allowed to set for several minutes, the samples were hung in a cabinet to dry.

Upon drying the samples were cut into strips approximately one inch wide and appropriately labelled so as to identify each strip as being a particular treatment combination.

Samples of each coated combination were processed in surface image developer MAA-1 (James, 1953) for 15, 30, and 45 minutes at 24 degrees Celsius as soon as a set of samples were dry. Samples within a given development time series were developed in a single tray to minimize the variability between time, temperature, agitation, and solution volume that might be present between trays. Following development the samples were placed in an acetic acid stop bath, and subsequently fixed in Kodak F-24 fixer, washed and dried.

The processed strips were examined densitometrically on a Macbeth TD-944 densitometer for evidence of the enhancement of reduction fog as might have been caused by the interstitial migration of gold to the sites of development. The measured density of the coated emulsions which were only gold sensitized was taken to be a control level of density for each given time of processing. The densitometric data from these samples are tabled in Appendix H.

Two additional sets of samples were sensitometrically exposed on an Automatic Type 1B, Model IV, Eastman Intensity Scale Sensitometer to determine what sensitometric effects any gold incorporated in the silver bromide crystals might have had. These samples were processed in trays for seven and a half minutes at 26.7 degrees Celsius in MAA-1 developer. The remainder of the processing schedule for the sensitometrically exposed samples was identical to that of the samples that had received no exposures prior to processing. The sensitometric data from these strips is tabled in Appendix I.

3.0 DISCUSSION

3.1 SENSITOMETRIC RESULTS

Evidence for the existence of migratory gold ions in a silver bromide emulsion would have been manifest in the form of significant density increases in all processed samples consisting of gold plus reduction over those that employed gold alone.

The unexposed high internal gold + surface reduction sensitization treatment combinations displayed greater average maximum densities than did the unexposed high internal gold alone at all development times (Table 15, Appendix H). The fog densities of the unexposed internal low gold plus reduction treatment combinations were higher than that of the samples not reduction sensitized in the fifteen and 45 minute development series. These data could be interpreted as evidence of the successful incorporation of gold ions in the cores of the grains and the subsequent migration of those ions to surface sites that were enhanced by reduction sensitization. However, the averaged results for all unexposed sample sets developed for thirty minutes were contrary to this.

The encouraging results from the unexposed samples

of gold plus reduction contrast sharply with the ineffectiveness of reduction sensitization as a density increasing agent on the unexposed samples for all times of development in MAA-1 when not used in combination with another sensitizer. The lack of any evidence of reduction sensitization in the otherwise unsensitized samples could be due to inadequate chemical treatment with stannous chloride, a lack of activity in the MAA-1 developer, or a combination of both. The MAA-1 developer may not have been powerful enough to enhance the relatively small speed differences between most treatment combinations.

If non-migratory gold had been successfully incorporated into the cores of the core/shell grains no density differences attributable to surface development would have existed between the gold and gold plus reduction sample sets. The density differences between the treatment combinations processed without exposure indicate that the most development took place in samples that were both gold and reduction sensitized. However, the results for the sensitometrically exposed treatment combinations show no trends clearly.

The poor response of the unexposed reduction

sensitized samples could be due to the partial neutralization of the stannous chloride reducing agent by a residual amount of hydrogen peroxide in the gelatin. It is also possible that the stannous chloride employed in the reduction sensitizations was slightly oxidized and was an ineffective agent of reduction sensitization. Any oxidation of stannous chloride would render the compound less active as an agent of reduction. The appearance of unoxidized stannous chloride is clear and the compound becomes increasingly opaque as oxidation progresses. The effectiveness of the stannous chloride used could be called into question by the results obtained from the sensitometrically exposed treatment combinations.

A partially successful reduction sensitization may have imparted a slight speed increase to all samples so treated. Even less reduction could have been effective at increasing density only in those treatments that were previously sensitized with gold that were free to migrate or reached the grain surfaces by some other means and were subject to relatively long times of development. These conditions would be met within the experimental design carried out only by the unexposed gold plus reduction treatment combinations.

A full development time series on the full design would be the surest way of deducing the effectiveness of the sensitizations carried out. A full development series was not carried out on the exposed samples when it was found that longer development times greatly accentuated the variability of the coatings prepared during preliminary work. The unexposed samples, being slower to develop, had more uniform density characteristics than did the exposed samples and were taken to be more reliable indicators of sensitization characteristics of the emulsions prepared than were exposed samples.

If the stannous chloride reduction sensitization was completely unsuccessful there may have still been a small amount of reduction taking place due to the use of formaldehyde as a hardening agent. If formaldehyde was the only effective agent of reduction sensitization then there should be no detectable differences between the treatment combinations that were distinguished from each other only by the presence or absence of reduction sensitization. The lack of speed increases for the reduction only treatment combinations over the unsensitized core/shell does not support the position

that the intended reduction of some samples was successful. Octahedral emulsions of the size prepared for the experiments can be reduction sensitized and the absence of any speed difference between the blank and the blank plus reduction was not expected.

The disparity of results between the low and high gold treatment combinations where the low gold combinations produced greater densities than their high gold counterparts in all treatment combinations can not be easily explained away. The high gold sensitizations may not have been as effective as the sensitizations for the low gold. The numbers of prelatent image sites created by the surface reduction of the silver bromide crystals should be the same for all classes of samples. Competition between development sites could be responsible but latent image failure due to oversensitization by the high gold treatments would require an emulsion with very few potential latent image sites. That is not a characteristic normally associated with core/shell emulsions.

Unperceived variables may have contributed to the densitometric anomalies extant in the low and high gold sample sets. The viscosity of the emulsion being

delivered to the coating head, web transport speed during coating, or an overheated Harvard Drive syringe system that delivers the liquified emulsion to the coating head employed could have all contributed to physical differences between the coated samples.

The experimental data (Tables 4-15, Appendix H) are, therefore, not fully supportive of the migration of gold ions in silver bromide crystal lattices. Because of inconsistencies between the samples treated with the low and high levels of gold, and because the stannous chloride treatments did not seem to be effective for any of the treatments, the hypothesis that gold ions might be mobile species was not provable within these experiments.

3.2 REACTION OF GOLD ION WITH GELATIN

The effectiveness of the use of oxidized as versus normal gelatin as a means of decreasing the tendency of gold ions to be reduced to the metallic state was gauged by comparing the absorptance spectrum of the gold sensitizer in solution to the spectra of the same compound when it was dispersed in both types of gelatin (Tables 28-36). These spectra were compared to additional spectra run on the same samples at a later date and indicated that the gelatin oxidation process had hindered the reduction of ionic gold. Gold(I) remained the predominant form of gold in the oxidized gelatins where the unoxidized gelatins had reduced the gold to a pinkish metallic dispersion (Harbison, 1991). The small amount of hydrogen peroxide used to reduce the gelatins was deemed sufficient to oxidize the gelatin based on the levels used by Maskasky (Maskasky, 1987) but inadequate to significantly affect the sensitization of the silver bromide during later stages of the experiment.

The use of oxidized phthalated gelatin throughout the nucleation and growth stages of the experiments should have decreased the undesirable complexation of

gold by the methionine groups which make up approximately one percent of gelatin. This statement is supported by work by Maskasky (Maskasky, 1987) but cannot be further substantiated by any work carried out during this set of experiments. Atomic absorption spectra would have been useful as a means of determining which gold-gelatin complexes if any had been formed during and after the application of gold sensitization.

3.3 IDEAS FOR POSSIBLE ADDITIONAL WORK

A lack of solution physical development associated with developers containing silver halide solvents could result in reduced development in the reduction sensitized treatment combinations (Haist, 1979). A solution physical developer might have amplified the effects of both the gold and reduction sensitizations. The comparison of the results obtained with a surface developer could have been contrasted with those of an internal developer.

A full development time series might have been done and more levels of both gold(III) and stannous chloride employed. A means of handling multiple sample sets in the dark so as to insure equal access to the developer solution for each sample of each treatment combination would have been useful.

Future experiments might include repeating the experimental scheme, or selected portions of it, with sulfur sensitization as an additional variable. Sulfur would have a strong localization effect on any migratory gold and provide gold ion traps at selected

depths within the bodies of the octahedra or other morphologies employed. If applied during crystal growth sulfer sensitization would most likely have a negative effect on the surface speed of an emulsion with a gold sensitized core. An emulsion with a gold sensitized core and surface sulfer sensitization might display a speed increase above that of the corresponding emulsion that was only sulfur sensitized due to the migration and subsequent incorporation of gold ions in the sulfur sensitized sites.

A gold sensitization matrix of different emulsions might be carried out with multiple levels of gold sensitization on cores of multiple sizes that are grown to the same finish size. Such a study might determine whether or not a time dependency exists for the migration of ionic gold from the grain interior to the surface the gold-rich zone which may exist below the surface of the shell.

The effectiveness of different gold sensitizing compounds might be evaluated as sources of incorporable gold ion for possible application to this type of study.

4.0 Appendices

4.1 Appendix A

Program VAg

This is the program written by the author to determine the potential of silver in an emulsion during the precipitation process from the input voltage potential of the system. This version is compatible with BASIC programmable calculators. The required inputs are the temperature of the system in degrees centigrade, and either a measured voltage potential of the system, or the desired potential of silver. The program can accept either VAg or pAg as input. The other variable is output. Depressing the ENTER key cycles the program back through the loop being utilized.

```
1: "V": REM VAG
2: PAUSE "VAG"
3: INPUT "TEMP?";T
4: T=T+273
5: K=K*.1
6: Pause "PAG/VAG"
7: INPUT "1 OR 2?";J
8: IF J=2 GOTO 14
   9: INPUT "PAG?";P
  10: P=T*P*.1984
  11: V=602-K-P
  12: PRINT "VAG=";V
  13: GOTO 9
14: INPUT"VAG?";V
15: P=(V-602+K)
16: P=P/(-.1984*T)
17: PRINT "PAG=";P
18: GOTO 14
```

4.2 Appendix B

Figure 1

Ramp Routine for the Nucleation
and Growth of .16 micron Cores
Using .66 Molar Solutions of Silver
Nitrate and Potassium Bromide

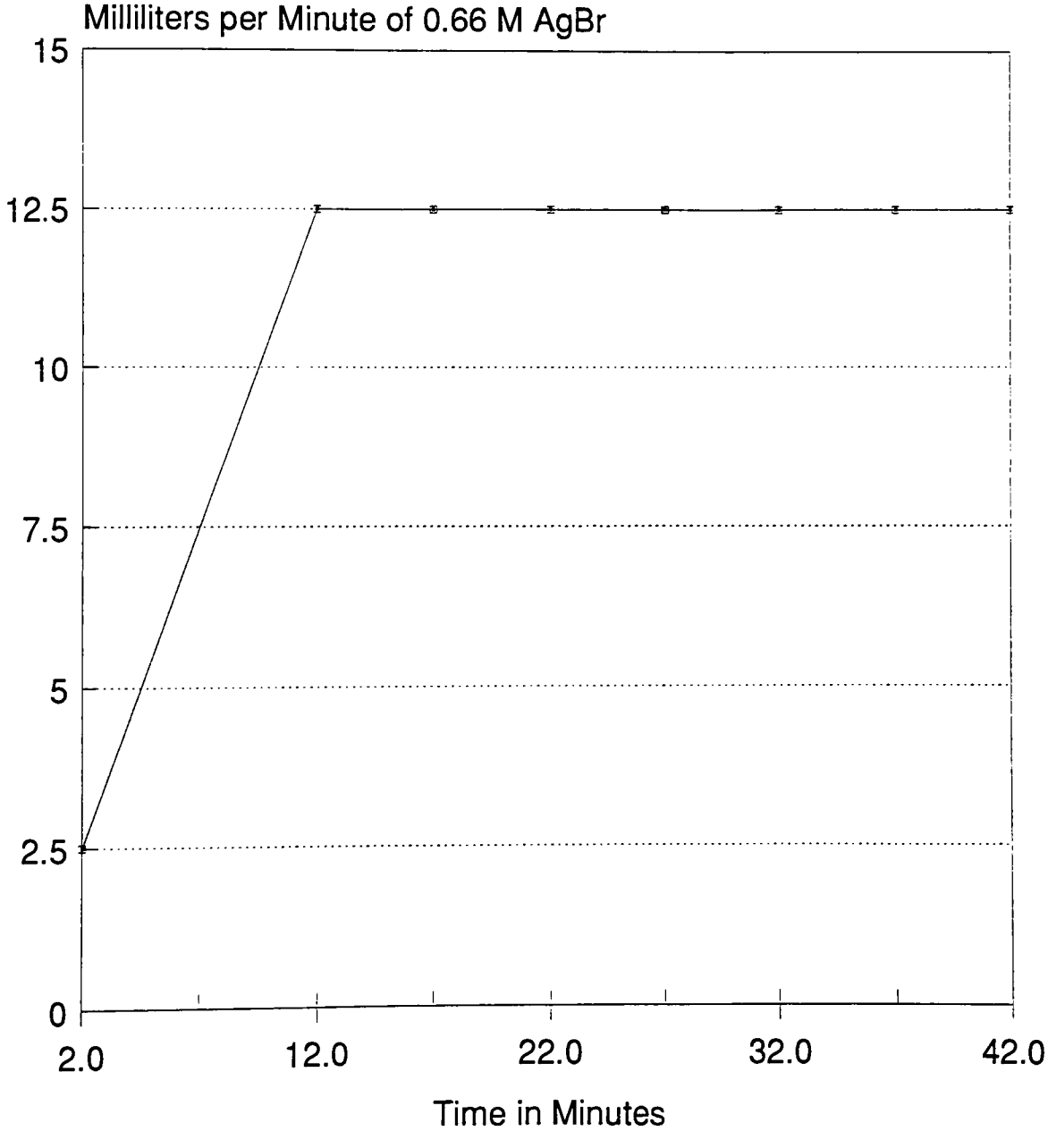
Program Board Set Up:

Solution	Pump	Milliliters per Minute Flow		
$AgNO_3$	01	2.50	2.50	10.30
KBr	02	2.54	2.54	10.46
time		2:00	7:45	

4.3 Appendix C

Figure 2

Profile of the Thesis Ramp Routine



4.4 Appendix D

Figure 3

Ramp Routine for Growth One Quarter Fractions of the .16 micron Core Emulsion to .32 micron Using .66 Molar Solutions of Silver Nitrate and Potassium Bromide

Program Board Set Up:

Solution	Pump	Milliliters per Minute Flow		
$AgNO_3$	01	2.575	3.125	3.125
KBr	02	2.616	3.175	3.175
time		2:15	29:12	

4.5 Appendix E

The Relationship Between the Time of Precipitation Under Conditions Approximating those of the Thesis and the Physical Parameters of the Emulsion Being Grown.

0.444 Liters run in x 0.66 Moles $AgNO_3$/Liter = 0.293 Moles Silver.

The formula for calculating the volume of octahedra is $0.47140 \times (\text{Diameter}/2) \times 2^{1/2}$

For an octahedra 0.32 microns in diameter:
$V = 0.4714(.16)(1.414) = 0.0054588 \text{ micron}^3$

and a mole of silver bromide has an approximate volume of $2.89825 \times 10^{13} \text{ microns}^3$ (see Appendix G).

Therefore 0.293 M AgBr x 2.89825×10^{13} microns^3 per Mole = 8.49304×10^{12} microns^3 of AgBr in the system.

8.49304×10^{12} microns^3 AgBr / 0.0054588 micron^3 / crystal

1.5558×10^{15} crystals of .32 micron diameter in the system.

For a constant number of silver bromide octahedra it follows that the:

(microns^3/Mole) x (Moles in the system) = Total microns^3

Total microns^3 / The number of crystals precipitated= microns^3/crystal

The diameter of octahedra = $3^{1/3} \times (\text{microns}^3 / 0.4714)^{1/3}$

Octahedra surface area = $3.46410 \times ((\text{microns}^3 / 0.4714)^{1/3})^2$

and

Octahedral surface area x 1.5558×10^{15} crystals = The total surface area of the emulsion at that point in time.

These formulae were used to generate the data shown in Table 2.

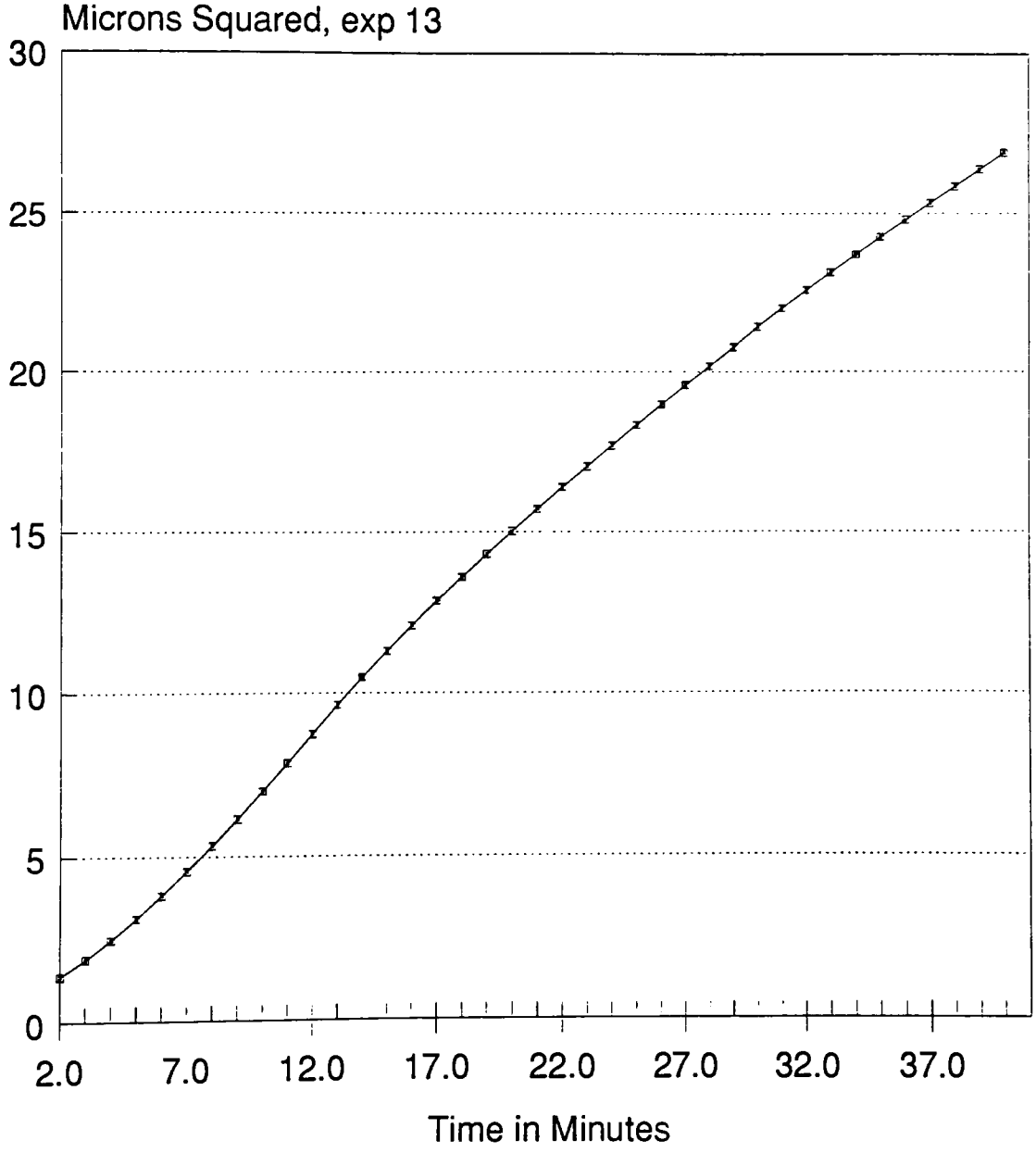
Table 2

The Calculated number of Moles of Silver Bromide, Volume per Crystal Microns^3, Surface Area per Crystal in Microns^2, and the Total Surface Area within an Emulsion Approximating Thesis Conditions at one Minute Intervals During Precipitation

Time	Moles	microns^{3}x10^5 crystal	microns^2 crystal	microns^{2}x10^{13} emulsion
2.0	.0033	6.25543	.00901236	1.3779
3.0	.00528	10.00086	.01232865	1.8850
4.0	.00792	15.0130	.01615511	2.4700
5.0	.01122	21.2684	.020378	3.1156
6.0	.01518	28.7750	.024927	3.8112
7.0	.01980	37.5326	.029758	4.5498
8.0	.02508	47.5413	.03483733	5.3264
9.0	.03102	58.8011	.04014096	6.1373
9.75	.03591	68.0669	.04432709	6.7773
10.0	.03762	71.3119	.04564982	6.9795
11.0	.04488	85.0739	.05134856	7.8508
12.0	.05280	100.0869	.05722456	8.7492
13.0	.06105	115.7255	.06304011	9.6384
14.0	.06930	131.3641	.06859861	10.4882
15.0	.07755	147.0027	.07394027	11.3049
16.0	.08580	162.6413	.07909543	12.0931
17.0	.09405	178.2799	.08408768	12.8564
18.0	.10230	193.9185	.08893587	13.5977
19.0	.11055	209.5571	.09365528	14.3192
20.0	.11880	225.1957	.09825865	15.0231
21.0	.12705	240.8343	.10256576	15.7108
22.0	.13530	256.4729	.10715811	16.3872
23.0	.14355	272.1115	.11147102	17.0431
24.0	.15180	287.7501	.11570304	17.6900
25.0	.16005	303.3886	.11985706	18.3253
26.0	.16830	319.0272	.12394127	18.9497
27.0	.17655	334.6658	.12795924	19.5641
28.0	.18480	350.3044	.13191509	20.1689
29.0	.19305	365.9431	.13581249	20.7648
30.0	.20130	381.5817	.14010389	21.4209
31.0	.20955	397.2200	.14390234	22.0017
32.0	.21780	412.8588	.14765114	22.5748
33.0	.22605	428.4974	.15135280	23.1408
34.0	.23430	444.1360	.15500960	23.6999
35.0	.24255	459.7746	.15862364	24.2524
36.0	.25080	475.4131	.16219684	24.7986
37.0	.25905	491.0517	.16573100	25.3391
38.0	.26730	506.6903	.16922775	25.8737
39.0	.27555	522.3289	.17268863	26.4029
40.0	.28380	537.9675	.17611507	26.9268

Figure 4

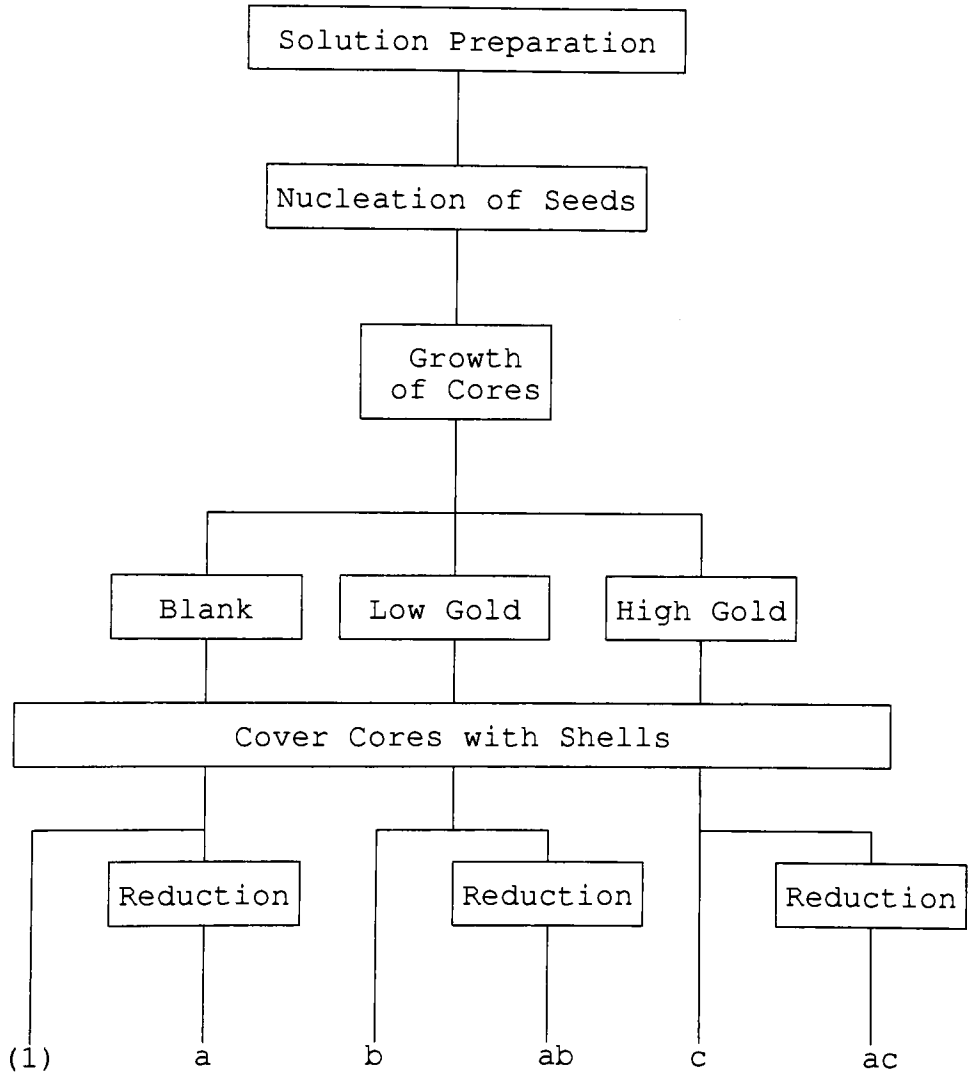
Total Surface Area vs. Time
Thesis Conditions



4.6 Appendix F

Figure 5

Flowchart of Experiment



4.7 Appendix G

The Relationship Between Crystal Surface Area and Crystal Size

For octahedra of any given size class:

Surface Area = Constant Radius

Therefore:

S_1 = Constant $Radius_1$

and

S_2 = Constant $Radius_2$

It then follows that:

$$S_1/S_2 = (K/R_1)/(K/R_2) = R_2/R_1$$

A Proof of the Above:

$$\frac{\text{surface area}}{\text{mole AgBr}} = \frac{\text{microns}^2}{\text{crystal}} \times \frac{\text{unit cells}}{\text{mole}} \times \frac{\text{microns}^3}{\text{unit cell}} \times \frac{\text{crystals}}{\text{microns}^3}$$

The four right hand terms above are:

$$\frac{\text{micron}^2}{\text{crystal}} = 3.4641 \times (1.414 \times \text{crystal radius})^2$$

$$\frac{\text{cells}}{\text{mole}} = \frac{6.02 \times 10^{23} \text{ atoms/mole}}{4 \text{ atoms Ag/cell AgBr}} = \frac{1.505 \times 10^{23} \text{ cells}}{\text{mole AgBr}}$$

$$\frac{\text{microns}^3}{\text{crystal}} = .4714 \times (1.414 \times \text{crystal radius})^3$$

$$\frac{\text{microns}^3}{\text{unit cell}} = \frac{(5.77475 \text{ angstroms})^3}{\text{unit cell AgBr}} = \frac{1.9257 \times 10^{-10} \text{ microns}^3}{\text{unit cell AgBr}}$$

Therefore:

$$\frac{\text{surface area}}{\text{mole AgBr}} = \frac{\text{microns}^2 \text{ / crystal}}{\text{crystal / microns}^3} \times \left[\frac{\text{unit cells}}{\text{mole}} \times \frac{\text{microns}^3}{\text{unit cell}} \right]$$

$$\left[\quad \right] \text{ reduces to } \left[\frac{2.898252 \times 10^{13} \text{ microns}^3}{\text{mole AgBr}} \right]$$

and

$$\frac{\text{microns}^2 \text{ / crystal}}{\text{microns}^3 \text{ / crystal}} = \frac{3.4641 \times (1.414(R))^2}{.4714 \times (1.414(R))^3}$$

Where R equals the maximum crystal radius in microns.

Which reduces to:

$$\frac{7.348536}{1.414(R)} = \frac{5.196985}{R}$$

$$\frac{5.196985}{R} \times \frac{2.898252 \times 10^{13} \text{ microns}^3}{\text{mole AgBr}} = \frac{1.506217 \times 10^{14} \text{ micron}}{\text{mole R octahedra}}$$

The equation above was used to generate Table 3.

Table 3
The relationship between crystal diameter and the surface area per mole of material

Octahedra diameter	microns^2/mole AgBr
.01 microns	3.012434×10^{16}
.02 "	1.506217×10^{16}
.04 "	7.531085×10^{15}
.08 "	3.765543×10^{15}
.16 "	1.882771×10^{15}
.32 "	9.413857×10^{14}
.64 "	4.706928×10^{14}
1.28 "	2.353464×10^{14}

It can therefore be safely stated that doubling crystal diameter effectively halves the surface area available for chemical sensitization per mole of material.

4.8 Appendix H

Densitometric Data

Table 4

Sample sets of January 28, 1990
Two strips each, 3 readings of each, streaks avoided.
Samples developed for 15 minutes

	Dmin						average	standard deviation
Blank	.04	.04	.04	.03	.03	.04	.037	.005
Blank+R	.04	.04	.04	.04	.04	.04	.04	.0
Low Gold	.08	.08	.09	.07	.08	.10	.08	.010
Low Gold+R	.10	.13	.09	.19	.17	.14	.137	.039
High Gold	.05	.04	.04	.05	.04	.06	.047	.008
High Gold+R	.04	.05	.05	.04	.05	.04	.045	.005

Table 5

Sample sets of January 28, 1990
Two strips each, 3 readings of each, streaks avoided.
Samples developed for 30 minutes

	Dmin						average	standard deviation
Blank	.05	.05	.05	.05	.05	.05	.05	.0
Blank+R	.04	.04	.04	.04	.05	.05	.043	.005
Low Gold	.15	.14	.14	.14	.19	.13	.15	.021
Low Gold+R	.13	.15	.11	.16	.12	.15	.14	.020
High Gold	.05	.07	.05	.05	.05	.06	.055	.008
High Gold+R	.06	.05	.04	.05	.05	.05	.05	.006

Table 6

Sample sets of January 28, 1990
Two strips each, 3 readings of each, streaks avoided.
Samples developed for 45 minutes

	Dmin						average	standard deviation
Blank	.07	.08	.08	.07	.08	.08	.077	.005
Blank+R	.06	.05	.06	.07	.06	.07	.062	.008
Low Gold	.19	.26	.21	.36	.37	.33	.287	.078
Low Gold+R	.28	.22	.31	.31	.27	.28	.28	.033
High Gold	.09	.08	.09	.10	.09	.07	.087	.010
High Gold+R	.11	.10	.10	.11	.16	.11	.115	.023

Table 7

Sample sets of January 22, 1990
One strip each, 3 readings of each, streaks avoided
Samples developed for 30 minutes

	Dmin			average	standard deviation
Blank	.04	.04	.04	.04	.0
Blank+R	.05	.04	.05	.046	.006

Table 8

Sample sets of January 22, 1990
Three strips each, 3 readings of each, streaks avoided
Samples developed for 90 minutes

	Dmin				average	standard deviation
Blank	.46	.45	.48			
	.41	.41	.39			
	.42	.50	.43		.44	.036
Blank+R	.37	.27	.26	(thin coating)		
	.58	.50	.50	.48		
	.58	.60	.64	.50	.48	.129

Table 9

Sample set 1 of February 2, 1990
Three strips each, 5 readings of each, streaks avoided
Samples developed for 15 minutes

	Dmin					average	standard deviation
Low Gold	.05	.06	.04	.06	.07		
	.06	.06	.06	.06	.05		
	.04	.05	.05	.05	.06	.055	.008
High Gold+R	.06	.06	.07	.03	.05		
	.07	.07	.06	.05	.07		
	.06	.09	.05	.05	.02	.057	.017

Table 10

Sample set 1 of February 2, 1990
Three strips each, 5 readings of each, streaks avoided
Samples developed for 30 minutes

	Dmin					average	standard deviation
Low Gold	.07	.08	.08	.06	.08		
	.14	.14	.15	.14	.12		
	.05	.05	.04	.07	.07	.089	.038
High Gold+R	.07	.07	.06	.05	.07		
	.16	.09	.10	.10	.17		
	.09	.10	.16	.11	.10	.10	.037

Table 11

Sample set 1 of February 2, 1990
Three strips each, 5 readings of each, streaks avoided
Samples developed for 45 minutes

	Dmin					average	standard deviation
Low Gold	.11	.10	.11	.12	.12		
	.12	.12	.11	.13	.10		
	.12	.15	.14	.14	.17	.124	.019
High Gold+R	.13	.11	.13	.08	.16		
	.13	.11	.14	.20	.11		
	.11	.12	.12	.12	.11	.125	.027

Table 12

Sample set 2 of February 2, 1990

Two to four strips each, 5 readings each, streaks avoided

Samples developed for 15 minutes

	Dmin					average	standard deviation
Low Gold	.03	.03	.03	.04	.03		
	.04	.05	.04	.04	.04		
	.04	.04	.03	.03	.04	.037	.006
Low Gold+R	.03	.03	.03	.03	.03		
	.03	.04	.03	.03	.03	.031	.003
High Gold	.03	.04	.03	.04	.04		
	.03	.03	.03	.03	.03		
	.03	.03	.04	.04	.04		
	.03	.03	.03	.04	.04	.034	.005
High Gold+R	.04	.04	.04	.03	.03		
	.04	.03	.03	.03	.03		
	.03	.03	.03	.04	.03	.033	.005

Table 13

Sample set 2 of February 2, 1990

Three to four strips each, 5 readings each, streaks avoided

Samples developed for 30 minutes

	Dmin					average	standard deviation
Low Gold	.03	.04	.04	.03	.03		
	.04	.04	.04	.04	.04		
	.04	.04	.03	.04	.04	.037	.005
Low Gold+R	.04	.04	.04	.04	.04		
	.05	.04	.03	.03	.04		
	.03	.03	.03	.04	.04	.037	.006
High Gold	.04	.04	.04	.04	.04		
	.04	.04	.04	.04	.04		
	.04	.03	.03	.04	.03		
	.03	.04	.04	.05	.04	.039	.005
High Gold+R	.04	.04	.04	.04	.04		
	.04	.04	.04	.04	.04		
	.04	.04	.03	.04	.04	.039	.003

Table 14
Sample set 2 of February 2, 1990
Four strips each, 5 readings each, streaks avoided
Samples developed for 45 minutes

	Dmin					average	standard deviation
Low Gold	.03	.03	.04	.03	.03		
	.05	.05	.04	.06	.06		
	.09	.18	.07	.17	.07		
	.13	.15	.13	.12	.13	.083	.050
Low Gold+R	.10	.11	.10	.11	.12		
	.12	.11	.14	.12	.17		
	.17	.09	.18	.19	.18		
	.09	.12	.13	.12	.10	.129	.031
High Gold	.15	.09	.15	.11	.09		
	.20	.20	.18	.15	.17		
	.12	.12	.13	.15	.15		
	.16	.20	.13	.16	.13	.147	.033
High Gold+R	.11	.14	.13	.15	.14		
	.11	.08	.09	.11	.08		
	.13	.13	.16	.15	.16		
	.05	.04	.07	.11	.06	.11	.037

Table 15
Grand Averages for All Sample Sets

Sample	Minutes of Development		
	15	30	45
Blank	.036	.05	.08
Blank+R	.04	.04	.06
Low Gold	.058	.093	.165
Low Gold+R	.083	.085	.205
High Gold	.038	.045	.114
High Gold+R	.056	.063	.117

4.9 Appendix I

Sensitometric Data

Sensitometric exposures were produced with one second exposures an Eastman 1B Sensitometer and processed for seven and one half minutes in the surface developer MAA-1 at 26.7 degrees Celsius.

Figure 6

Unsensitized Core/Shells

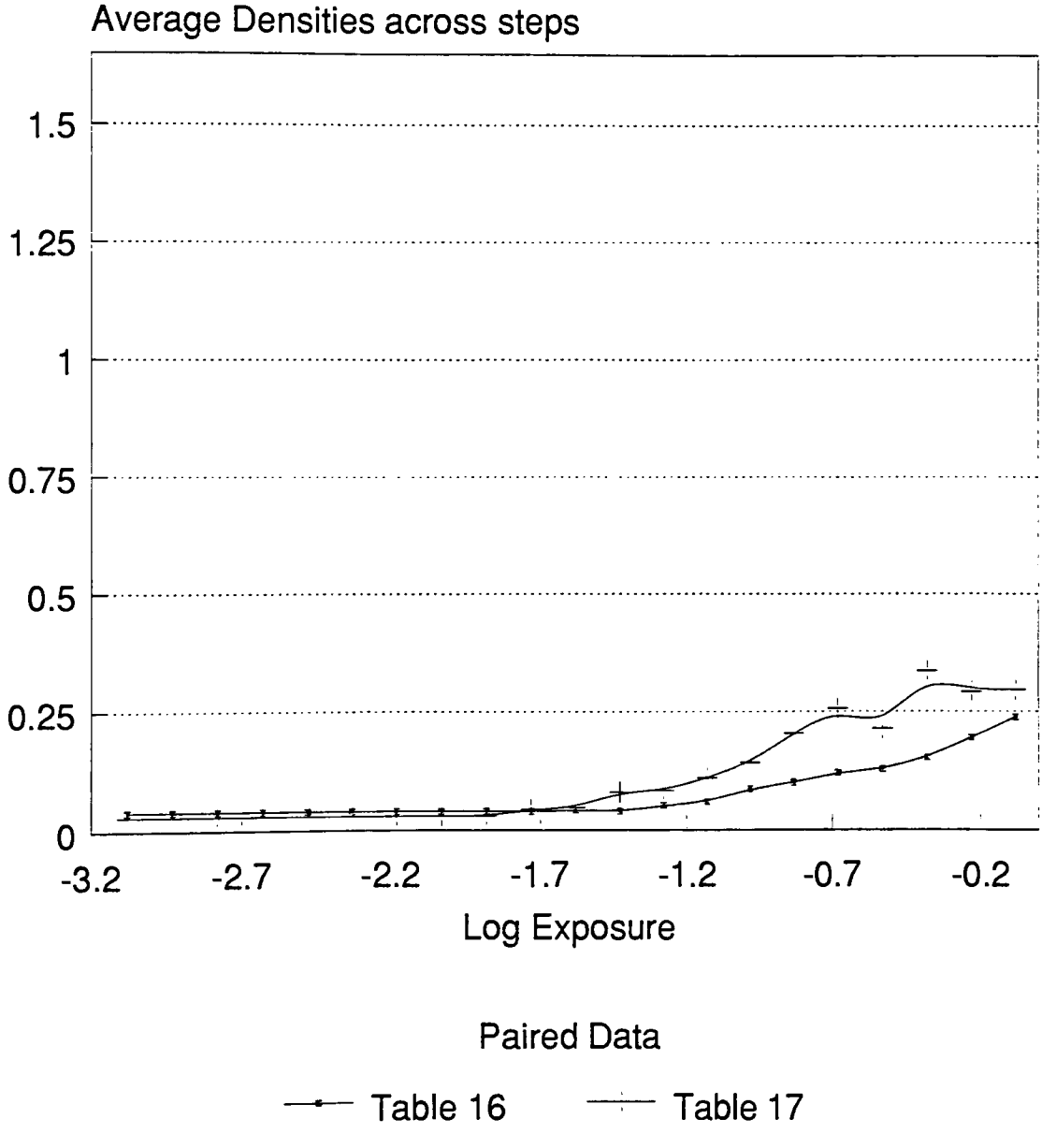


Figure 7

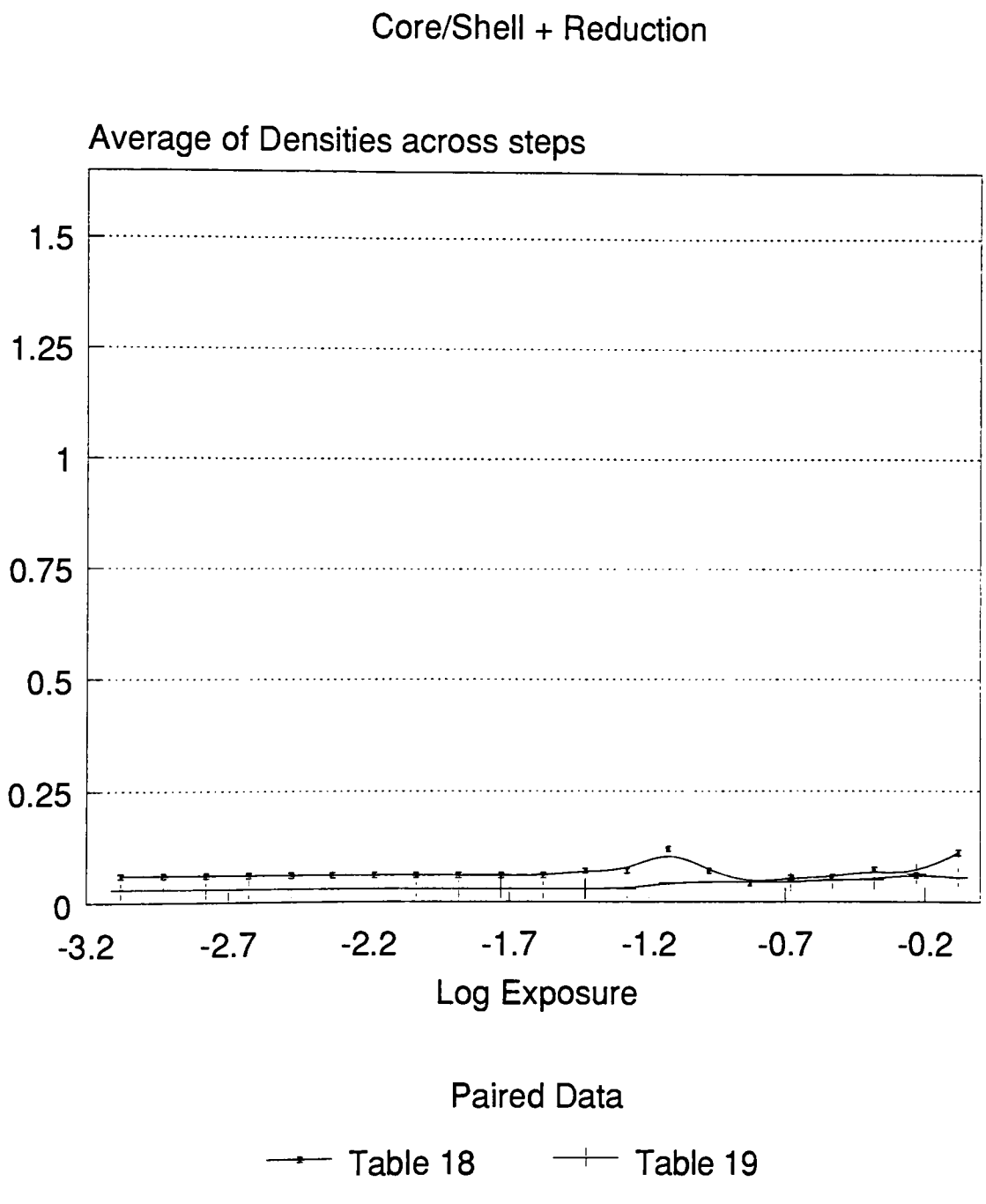

Core/Shell + Reduction
Average of Densities across steps
1.5
1.25
1
0.75
0.5
0.25
0
-3.2
-2.7
-2.2
-1.7
-1.2
-0.7
-0.2
Log Exposure
Paired Data
Table 18
Table 19

Figure 8

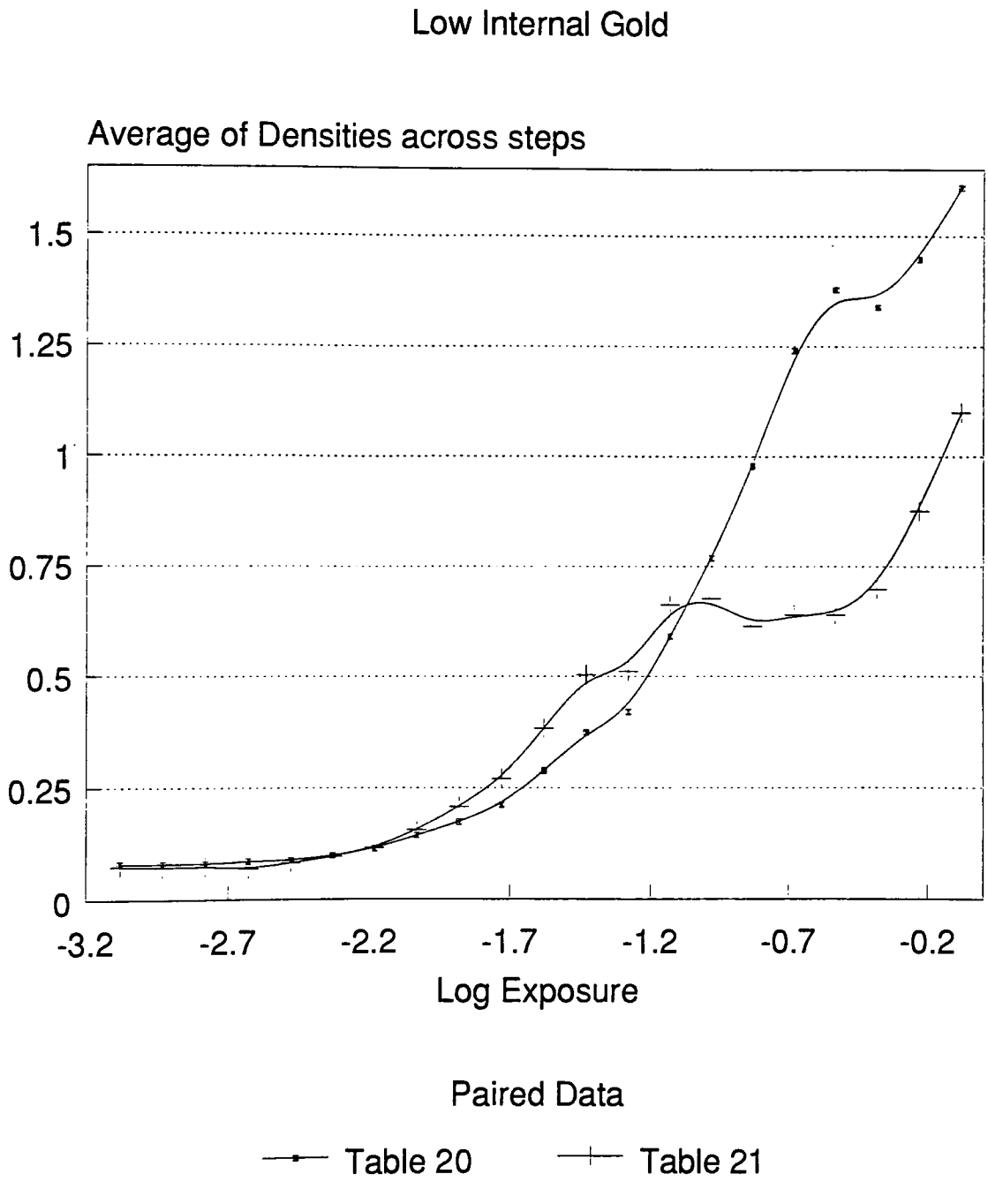

Low Internal Gold
Average of Densities across steps
1.5
1.25
1
0.75
0.5
0.25
0
-3.2
-2.7
-2.2
-1.7
-1.2
-0.7
-0.2
Log Exposure
Paired Data
Table 20
Table 21

Figure 9

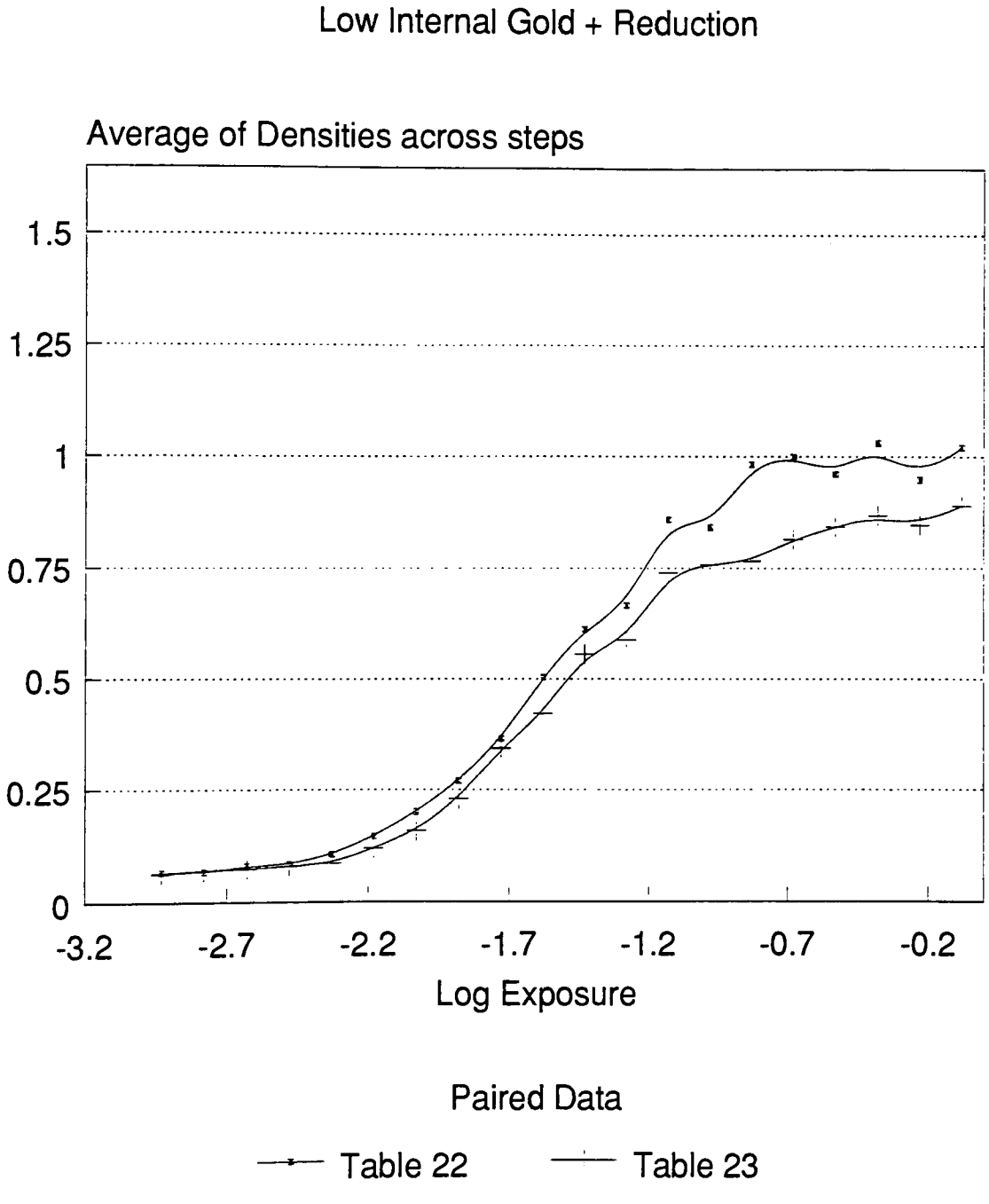

Low Internal Gold + Reduction
Average of Densities across steps
1.5
1.25
1
0.75
0.5
0.25
0
-3.2
-2.7
-2.2
-1.7
-1.2
-0.7
-0.2
Log Exposure
Paired Data
Table 22
Table 23

Figure 10

High Internal Gold

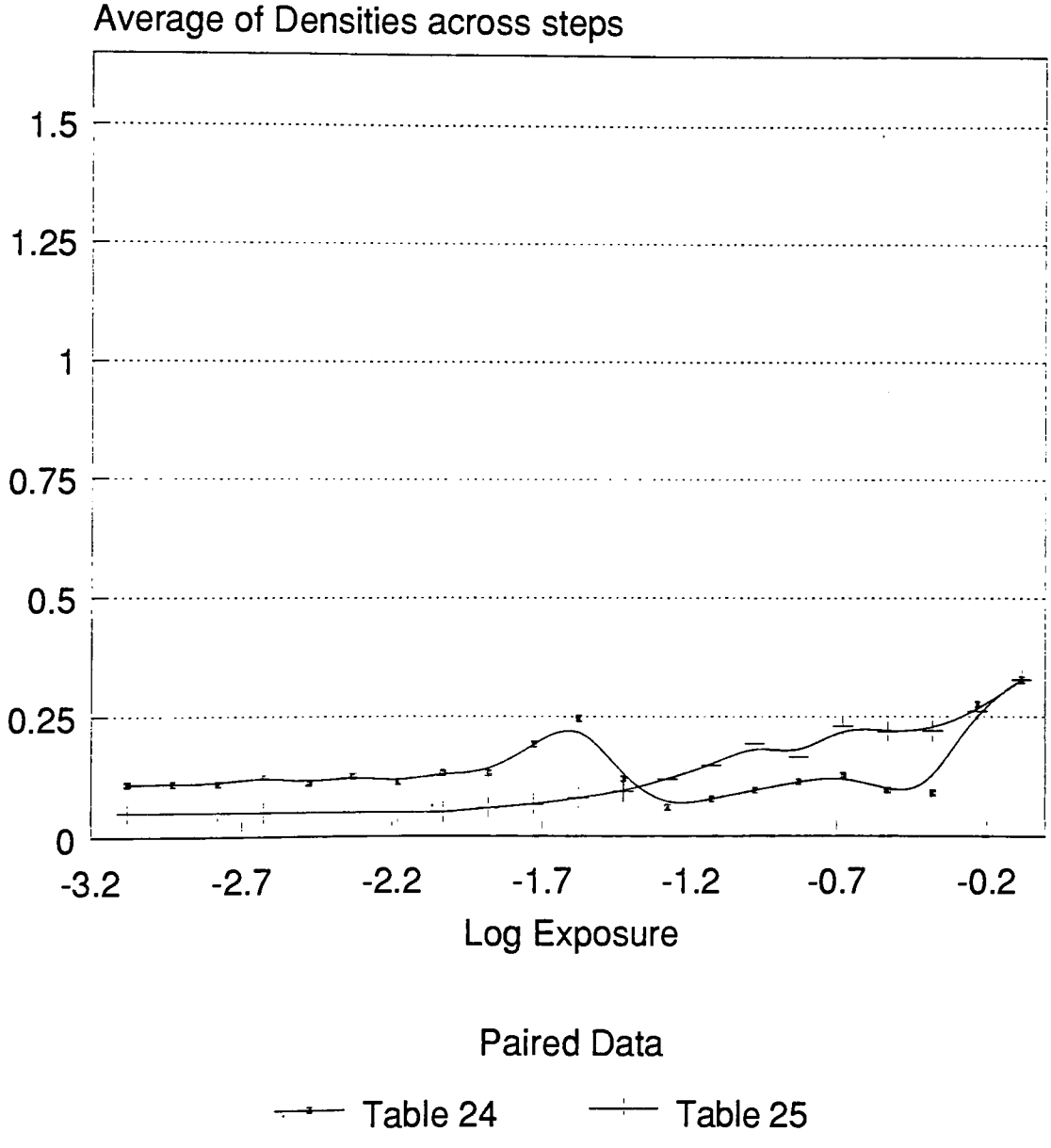


Figure 11

High Internal Gold + Reduction

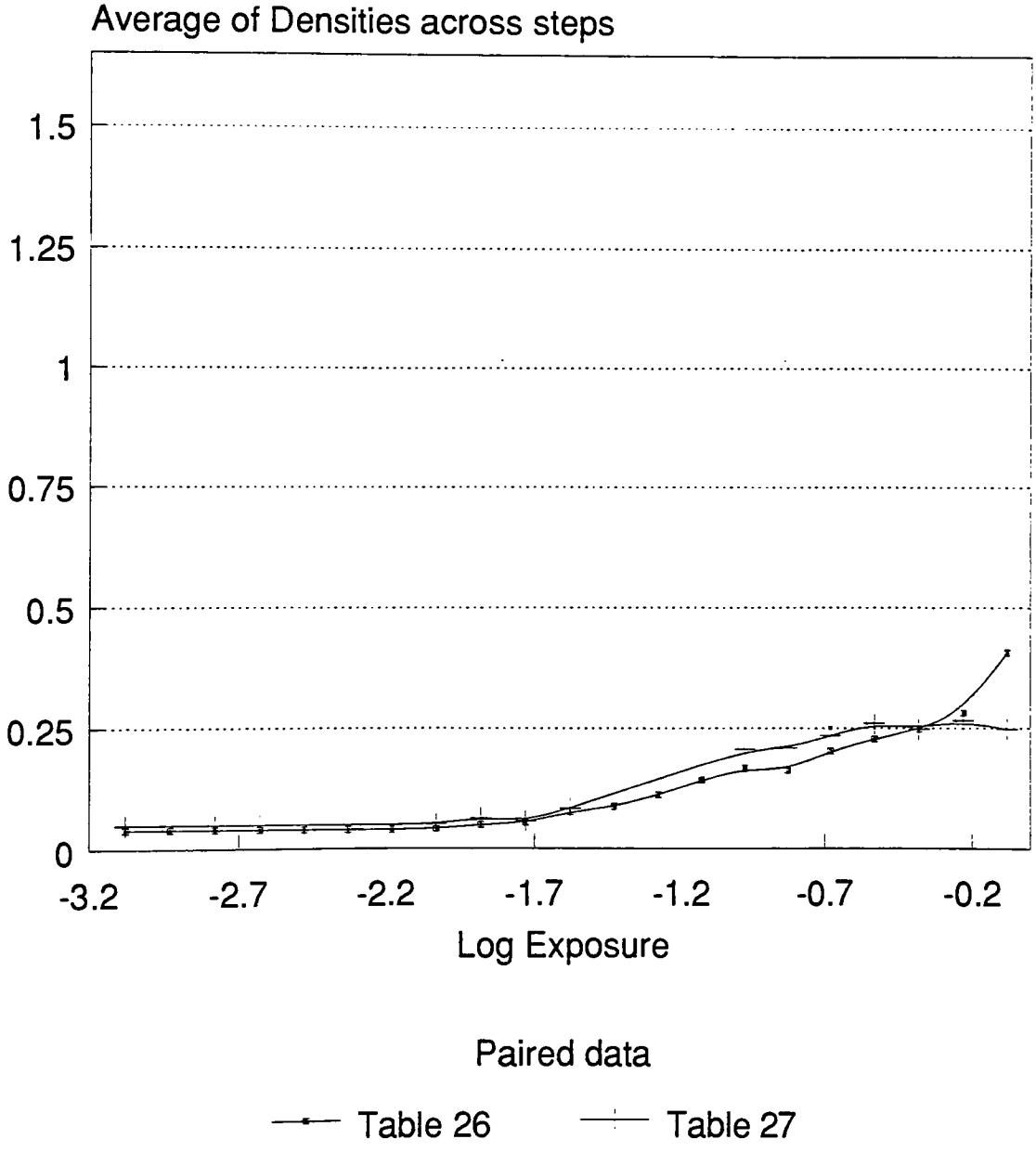


Table 16
Unsensitized Core/Shell
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.25	.24	.23	.23		.238	.010
20	-0.23	.17	.21	.17	.22	.20	.194	.023
19	-0.38	.14	.16	.16	.14	.16	.152	.011
18	-0.53	.12	.13	.13	.12	.14	.128	.008
17	-0.68	.13	.12	.12	.11	.12	.120	.007
16	-0.83	.09	.10	.10	.11		.100	.008
15	-0.98	.08	.09	.09			.087	.006
14	-1.13	.06	.06	.06			.060	.000
13	-1.28	.05	.05	.06	.05	.05	.052	.004
12	-1.43	.04	.04	.04	.04.	.04	.040	.000
11	-1.58	.04	.04	.04	.04	.05	.042	.004
10	-1.73							
9	-1.88							
8	-2.03							
7	-2.18							
6	-2.33							
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

Table 17
Unsensitized Core/Shell
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.28	.29	.29	.29	.33	.296	.019
20	-0.23	.28	.30	.30	.29	.29	.292	.008
19	-0.38	.31	.32	.34	.34	.37	.336	.023
18	-0.53	.22	.22	.21	.21	.21	.214	.005
17	-0.68	.26	.26	.24	.25	.27	.256	.011
16	-0.83	.21	.21	.20	.20	.20	.204	.005
15	-0.98	.14	.14	.14	.14	.15	.142	.004
14	-1.13	.11	.11	.11	.11	.11	.110	.000
13	-1.28	.08	.09	.08	.09	.08	.084	.005
12	-1.43	.08	.08	.08	.08	.08	.080	.000
11	-1.58	.05	.04	.05	.05	.05	.048	.004
10	-1.73	.03	.04	.05	.05	.05	.044	.009
9	-1.88	.03	.03	.03	.03	.03	.030	.000
8	-2.03							
7	-2.18							
6	-2.33							
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

Table 18
Blank plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.11	.09	.12	.12	.11	.110	.012
20	-0.23	.06	.05	.06	.07	.06	.060	.007
19	-0.38	.07	.08	.07	.07	.07	.072	.004
18	-0.53	.06	.05	.05	.05	.07	.056	.009
17	-0.68	.05	.06	.07	.04	.05	.054	.011
16	-0.83	.05	.03	.04	.05	.04	.042	.008
15	-0.98	.08	.07	.06			.070	.010
14	-1.13	.12	.12	.11	.12		.118	.005
13	-1.28							
12	-1.43							
11	-1.58							
10	-1.73							
9	-1.88							
8	-2.03							
7	-2.18							
6	-2.33							
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

Table 19
Blank plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements				Average	Standard deviation
21	-0.08	.06	.06	.05	.05	.055	.006
20	-0.23	.05	.07	.07	.06	.063	.010
19	-0.38	.04	.05	.06	.05	.050	.008
18	-0.53	.04	.05	.06	.05	.050	.008
17	-0.68	.04	.04	.05	.05	.045	.006
16	-0.83	.04	.05	.04	.05	.045	.006
15	-0.98	.04	.05	.05	.04	.045	.006
14	-1.13	.05	.04	.04		.043	.006
13	-1.28	.03					
12	-1.43						
11	-1.58						
10	-1.73						
9	-1.88						
8	-2.03						
7	-2.18						
6	-2.33						
5	-2.48						
4	-2.63						
3	-2.78						
2	-2.93						
1	-3.08						

Table 20
Low Internal Gold
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	1.69	1.61	1.61	1.51	1.62	1.61	.064
20	-0.23	1.36	1.52	1.50	1.45	1.39	1.44	.069
19	-0.38	1.45	.96	1.45	1.37	1.45	1.34	.213
18	-0.53	1.12	1.46	1.38	1.47	1.46	1.38	.149
17	-0.68	.77	1.43	1.37	1.35	1.27	1.24	.268
16	-0.83	.58	.98	1.03	1.30	1.00	.978	.258
15	-0.98	.52	.75	.83	.98	.76	.768	.166
14	-1.13	.31	.57	.70	.76	.61	.590	.173
13	-1.28	.34	.34	.53	.57	.32	.420	.120
12	-1.43	.38	.42	.38	.35	.34	.374	.031
11	-1.58	.32	.30	.28	.24	.30	.288	.030
10	-1.73	.20	.25	.25	.20	.16	.212	.038
9	-1.88	.10	.19	.19	.23	.16	.174	.048
8	-2.03	.17	.12	.14	.13	.16	.144	.021
7	-2.18	.10	.11	.12	.13	.11	.114	.011
6	-2.33	.09	.10	.10	.11	.09	.098	.008
5	-2.48	.07	.09	.09	.10	.09	.088	.011
4	-2.63	.08	.08	.09	.09	.09	.086	.006
3	-2.78	.08	.08	.08	.08	.08	.080	.000
2	-2.93							
1	-3.08							

Table 21
Low Internal Gold
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	1.12	1.12	.92	1.13	1.23	1.10	.113
20	-0.23	.90	.85				.875	.035
19	-0.38	.69	.71	.69			.697	.012
18	-0.53	.66	.61	.66	.63		.640	.024
17	-0.68	.68	.65	.61	.61	.65	.640	.030
16	-0.83	.71	.65	.61	.56	.54	.614	.069
15	-0.98	.88	.64	.65	.60	.61	.676	.116
14	-1.13	.78	.71	.64	.59	.59	.662	.082
13	-1.28	.56	.51	.51	.48	.50	.512	.029
12	-1.43	.52	.52	.51	.49	.48	.504	.018
11	-1.58	.38	.39	.36	.40	.39	.384	.015
10	-1.73	.25	.27	.31	.25	.27	.270	.024
9	-1.88	.19	.21	.22	.21	.21	.208	.011
8	-2.03	.15	.17	.16	.15	.15	.156	.009
7	-2.18	.11	.12	.12	.12	.11	.116	.005
6	-2.33	.09	.09	.10	.10	.10	.096	.005
5	-2.48	.07	.08	.08	.09	.09	.082	.008
4	-2.63	.06	.07	.07	.07	.08	.070	.007
3	-2.78	.07	.07	.07	.08	.08	.074	.005
2	-2.93	.07	.07	.08	.07	.07	.072	.004
1	-3.08	.07	.08	.07	.07	.08	.074	.005

Table 22
Low Internal Gold plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.97	1.01	1.01	1.12	.98	1.02	.060
20	-0.23	.94	1.00	.92	.92	.96	.948	.034
19	-0.38	1.05	1.05	1.04	.99	1.00	1.03	.029
18	-0.53	.97	.96	.92	.93	1.02	.960	.039
17	-0.68	1.05	1.04	.99	.92	1.01	1.00	.052
16	-0.83	1.01	.99	.99	.93	.99	.982	.030
15	-0.98	.89	.88	.85	.80	.78	.840	.049
14	-1.13	.92	.88	.84	.83	.82	.858	.042
13	-1.28	.64	.70	.66	.64	.69	.666	.028
12	-1.43	.62	.62	.63	.60	.59	.612	.016
11	-1.58	.50	.52	.49	.47	.54	.504	.027
10	-1.73	.40	.38	.36	.35	.34	.366	.024
9	-1.88	.27	.28	.26	.26	.28	.270	.010
8	-2.03	.22	.21	.20	.19	.18	.200	.016
7	-2.18	.16	.15	.15	.14	.13	.146	.011
6	-2.33	.11	.11	.10	.11	.10	.106	.006
5	-2.48	.09	.08	.09	.08	.08	.084	.006
4	-2.63	.08	.08	.08	.08	.08	.080	.000
3	-2.78	.07	.07	.06	.07	.07	.068	.005
2	-2.93	.06	.07	.07			.066	.006
1	-3.08	.06						

Table 23
Low Internal Gold plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.78	.96	.87	.93	.91	.890	.070
20	-0.23	.81	.85	.79	.86	.92	.846	.050
19	-0.38	.91	.86	.78	.85	.94	.868	.061
18	-0.53	.80	.87	.80	.83	.91	.842	.048
17	-0.68	.80	.81	.77	.80	.89	.814	.045
16	-0.83	.80	.80	.72	.75	.76	.766	.034
15	-0.98	.89	.77	.69	.67	.77	.758	.087
14	-1.13	.80	.77	.67	.69	.77	.740	.057
13	-1.28	.55	.64	.59	.62	.56	.588	.036
12	-1.43	.58	.59	.53	.58	.50	.556	.039
11	-1.58	.47	.42	.45	.36	.41	.422	.042
10	-1.73	.25	.27	.38	.39	.43	.344	.079
9	-1.88	.18	.20	.24	.26	.27	.230	.039
8	-2.03	.14	.12	.16	.18	.19	.158	.029
7	-2.18	.12	.09	.12	.13	.14	.120	.019
6	-2.33	.07	.05	.09	.11	.11	.086	.026
5	-2.48	.08	.06	.08	.09	.09	.080	.012
4	-2.63	.07	.06	.07	.08	.09	.074	.011
3	-2.78	.07	.06	.08	.06	.08	.070	.010
2	-2.93	.06	.05	.07	.08	.06	.064	.011
1	-3.08							

Table 24
High Internal Gold
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.34	.32	.32	.33	.33	.328	.008
20	-0.23	.28	.22	.27	.30	.31	.276	.004
19	-0.38	.09	.06	.11	.10	.09	.090	.019
18	-0.53	.11	.09	.10	.09	.09	.096	.009
17	-0.68	.12	.12	.13	.12	.14	.126	.009
16	-0.83	.11	.11	.11	.12	.12	.114	.006
15	-0.98	.09	.10	.09	.10	.10	.096	.006
14	-1.13	.08	.08	.08	.08	.07	.078	.005
13	-1.28	.06	.06	.06	.06	.06	.060	.000
12	-1.43	.17	.07	unevenly coated			.120	.071
11	-1.58	.21	.27	.29	.25	.21	.246	.036
10	-1.73	.19	.16	.19	.26	.16	.192	.041
9	-1.88	.15	.11	.18	.11	.11	.132	.032
8	-2.03	.14	.12	.15	.12	.13	.132	.013
7	-2.18	.12	.10	.15	.10	.10	.114	.022
6	-2.33	.13	.11	.12	.16	.11	.126	.021
5	-2.48	.11	.11	.13	.11	.10	.112	.011
4	-2.63	.11	.11	.13	.15	stain	.125	.019
3	-2.78	.11	.11	.11	.11	.11	.110	.000
2	-2.93							
1	-3.08							

Table 25
High Internal Gold
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.33	.41	.19	.38		.328	.097
20	-0.23	.33	.43	.26	.17	.12	.262	.124
19	-0.38	.37	.16	.10	.30	.17	.220	.111
18	-0.53	.36	.30	.12	.12	.19	.218	.108
17	-0.68	.33	.20	.15	.14	.33	.230	.094
16	-0.83	.11	.13	.20	.28	.11	.166	.074
15	-0.98	.13	.15	.22	.26	.20	.192	.053
14	-1.13	.11	.11	.19	.24	.09	.148	.064
13	-1.28	.09	.09	.15	.17	.10	.120	.037
12	-1.43	.08	.07	.12	.08	.12	.094	.024
11	-1.58	.07	.06	.11	.06	.10	.080	.023
10	-1.73	.06	.06	.09	.06	.05	.067	.020
9	-1.88	.06	.07	.06	.05		.060	.008
8	-2.03	.05	.05	.05			.050	.000
7	-2.18							
6	-2.33							
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

Table 26
High Internal Gold plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.41	.40	.42	.39	.41	.406	.011
20	-0.23	.25	.30	.34	.27	.25	.282	.038
19	-0.38	.24	.24	.26	.23	.27	.248	.016
18	-0.53	.23	.23	.22			.227	.006
17	-0.68	.21	.21	.19	.19	.21	.202	.011
16	-0.83	.16	.16	.17	.17	.15	.162	.008
15	-0.98	.17	.18	.15	.15	.18	.166	.015
14	-1.13	.16	.14	.14	.14	.13	.142	.011
13	-1.28	.12	.11	.11	.09	.13	.112	.015
12	-1.43	.09	.10	.08	.08	.09	.088	.008
11	-1.58	.09	.06	.08			.077	.015
10	-1.73	.06	.06	.05	.05	.05	.054	.006
9	-1.88	.05	.05	.05	.05	.05	.050	.000
8	-2.03	.05	.04	.04	.04	.04	.042	.005
7	-2.18	.04	.04	.04	.04	.04	.040	.000
6	-2.33	.04	.04	.04	.04	.04	.040	.000
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

Table 27
High Internal Gold plus Surface Reduction
Sample coatings of February 2, 1990
Five readings taken across strip

Step Number	Log Exposure	Density Measurements					Average	Standard deviation
21	-0.08	.25	.25	.24	.24	.26	.248	.008
20	-0.23	.25	.26	.28	.26	.27	.266	.009
19	-0.38	.24	.25	.24	.25	.26	.248	.008
18	-0.53	.25	.26	.27	.27	.25	.260	.010
17	-0.68	.19	.21	.28	.25	.24	.234	.035
16	-0.83	.22	.20	.20	.21	.21	.208	.008
15	-0.98	.19	.22	.20	.21	.21	.206	.011
14	-1.13	streaked						
13	-1.28	.30	.33	.32	.32	.32		
12	-1.43							
11	-1.58	.09	.08	.08	.08	.09	.084	.005
10	-1.73	.06	.05	.06	.06	.06	.058	.004
9	-1.88	.06	.06	.07	.07	.06	.064	.005
8	-2.03	.05	.05	.05	.06	.05	.052	.004
7	-2.18							
6	-2.33							
5	-2.48							
4	-2.63							
3	-2.78							
2	-2.93							
1	-3.08							

4.10 Appendix J

Spectrophotometric Data
Sample Absorbtances were Measured on an
IBM UV-Vis 9420 Spectrophotometer

Criteria:

Data mode	: %Absorbtance
Band width	: 2.00 nanometers
Time constant	: 0.4 seconds
Lambda set	: 900 to 200 nm
Delta lambda	: 50
Lambda scale	: 20 nm/cm
Scan speed	: 400 nm/minute
Cell	: Quartz

Figure 12

Inert Gelatin

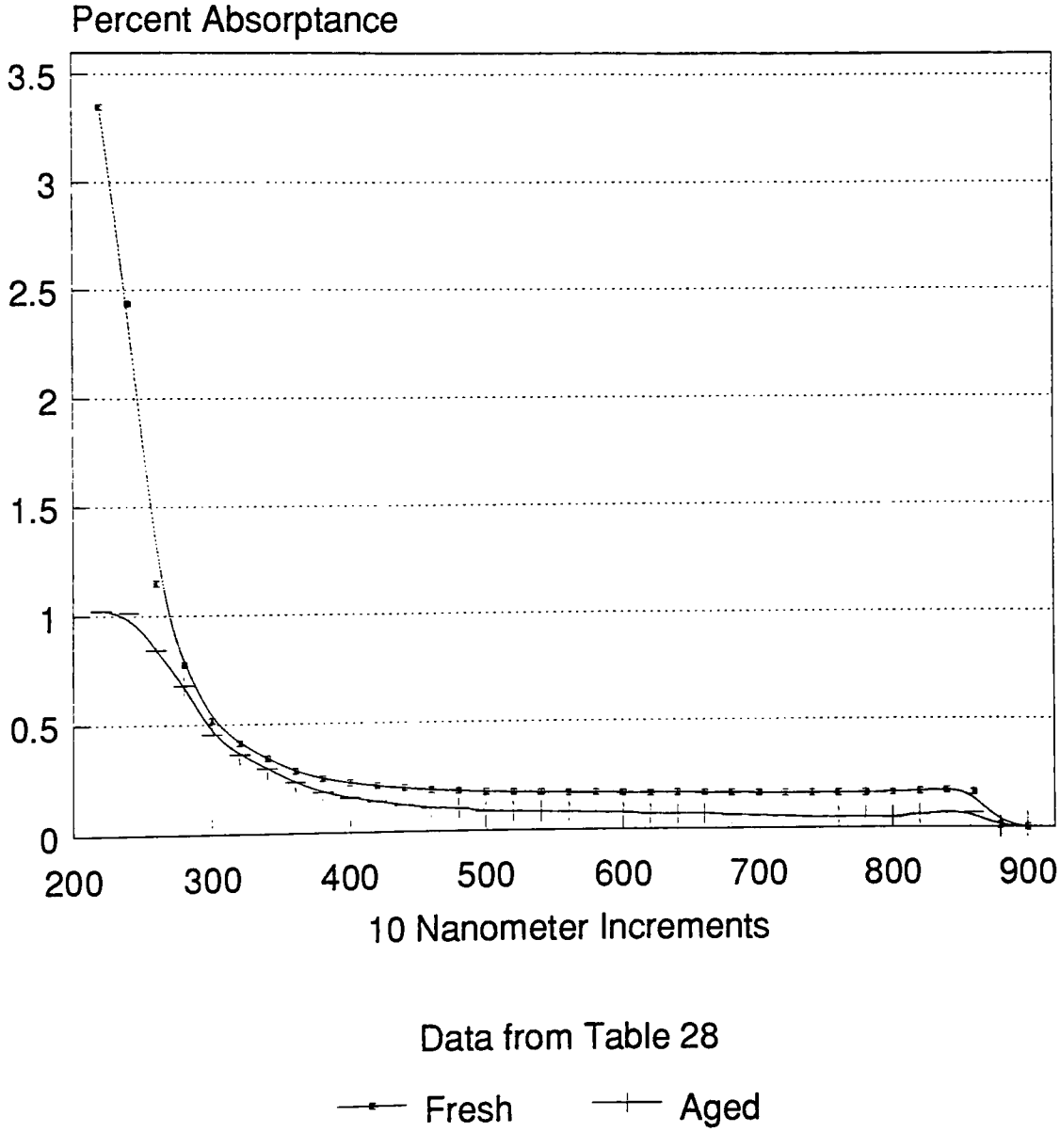


Figure 13

Oxidized Inert Gelatins

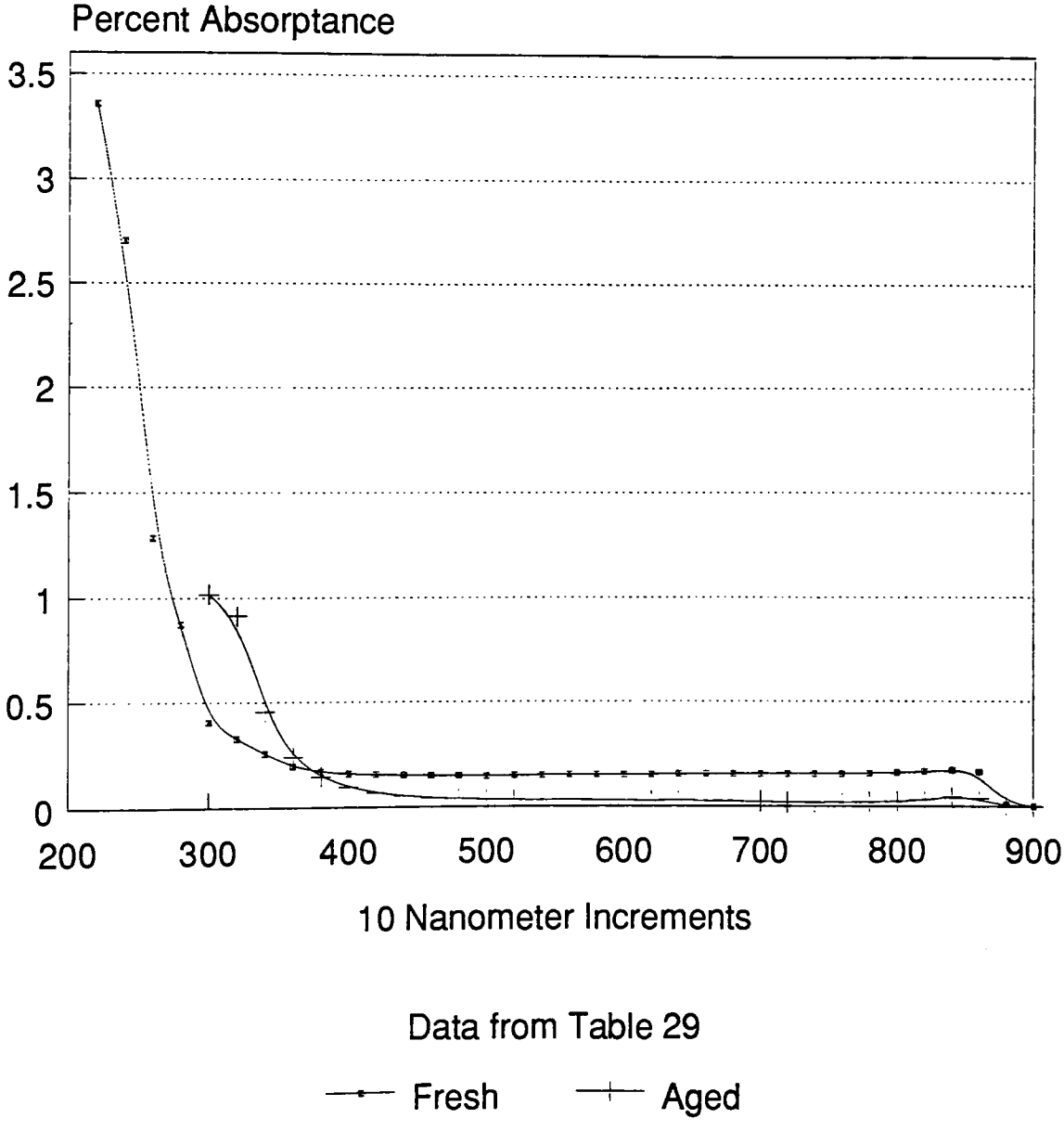


Figure 14

Phthalated Gelatins

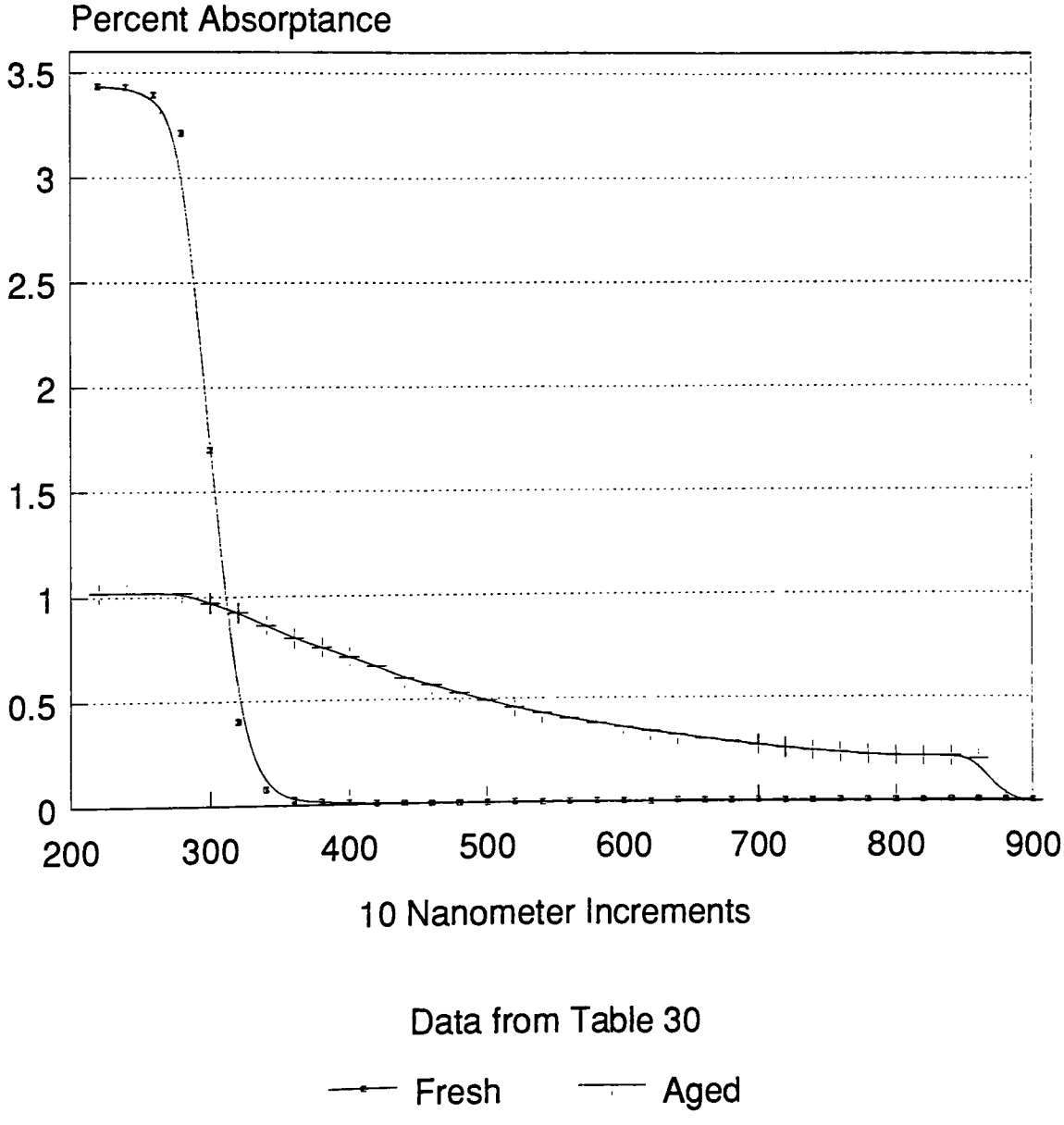


Figure 15

Oxidized Phthalated Gelatins

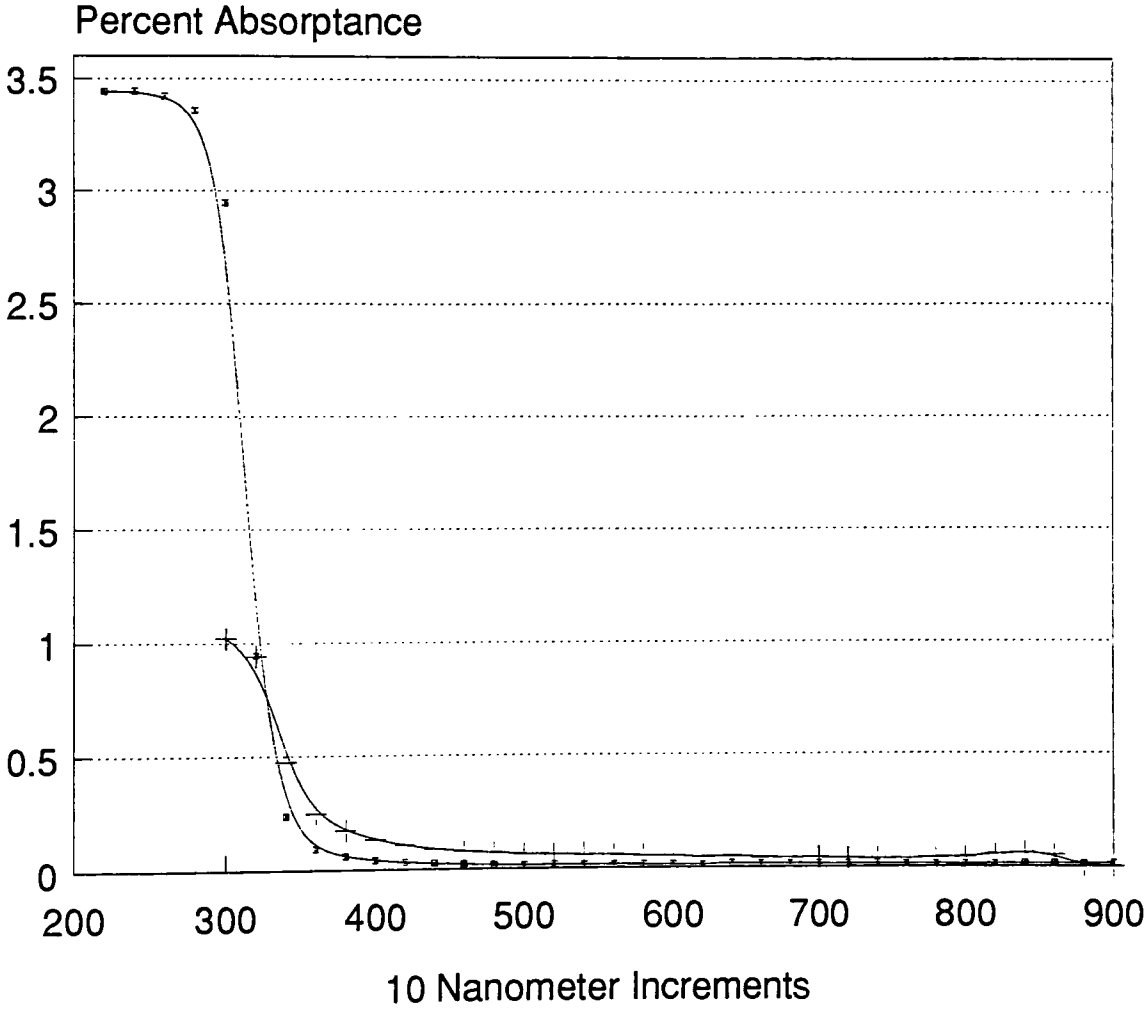


Figure 16

Inert Gelatins + Gold

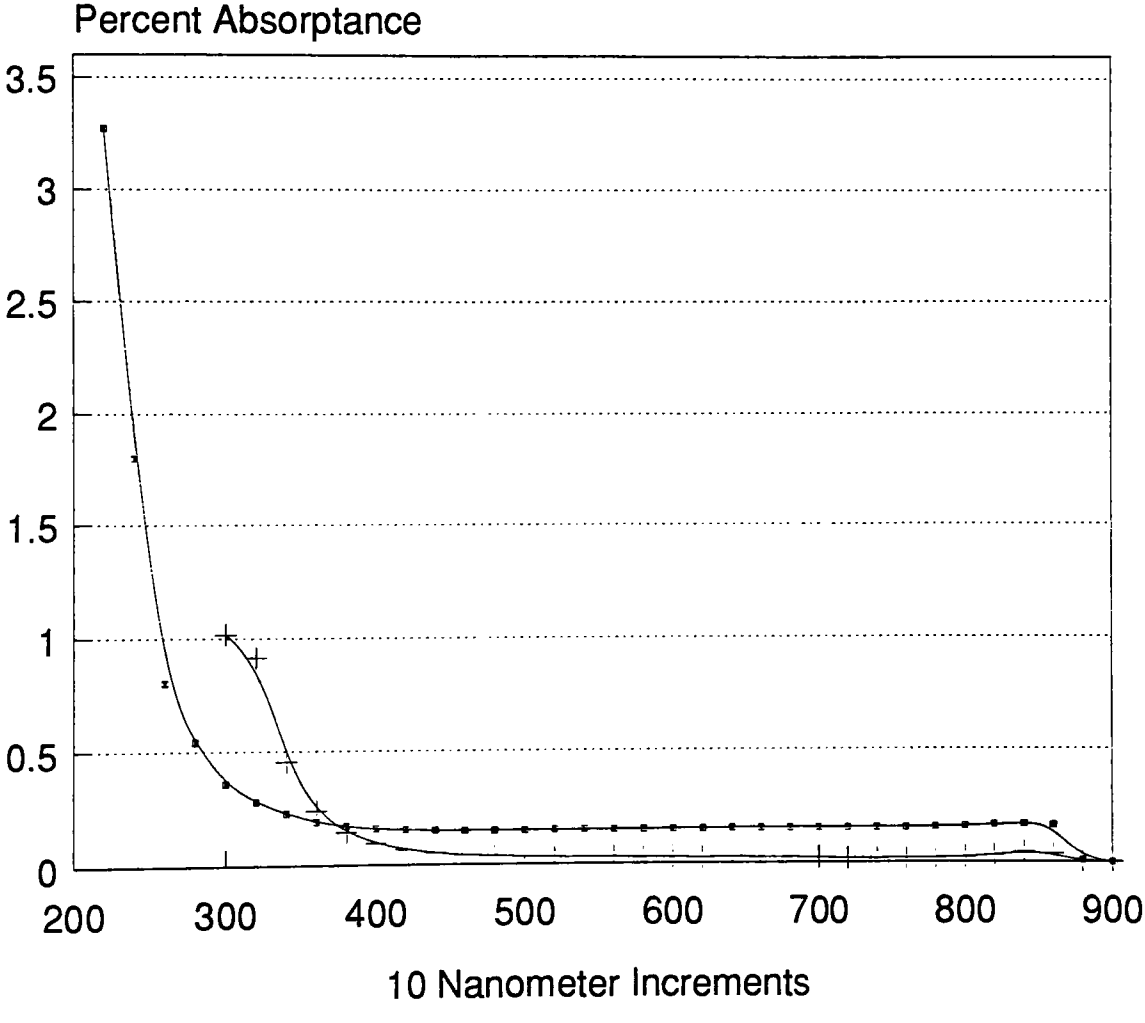


Figure 17

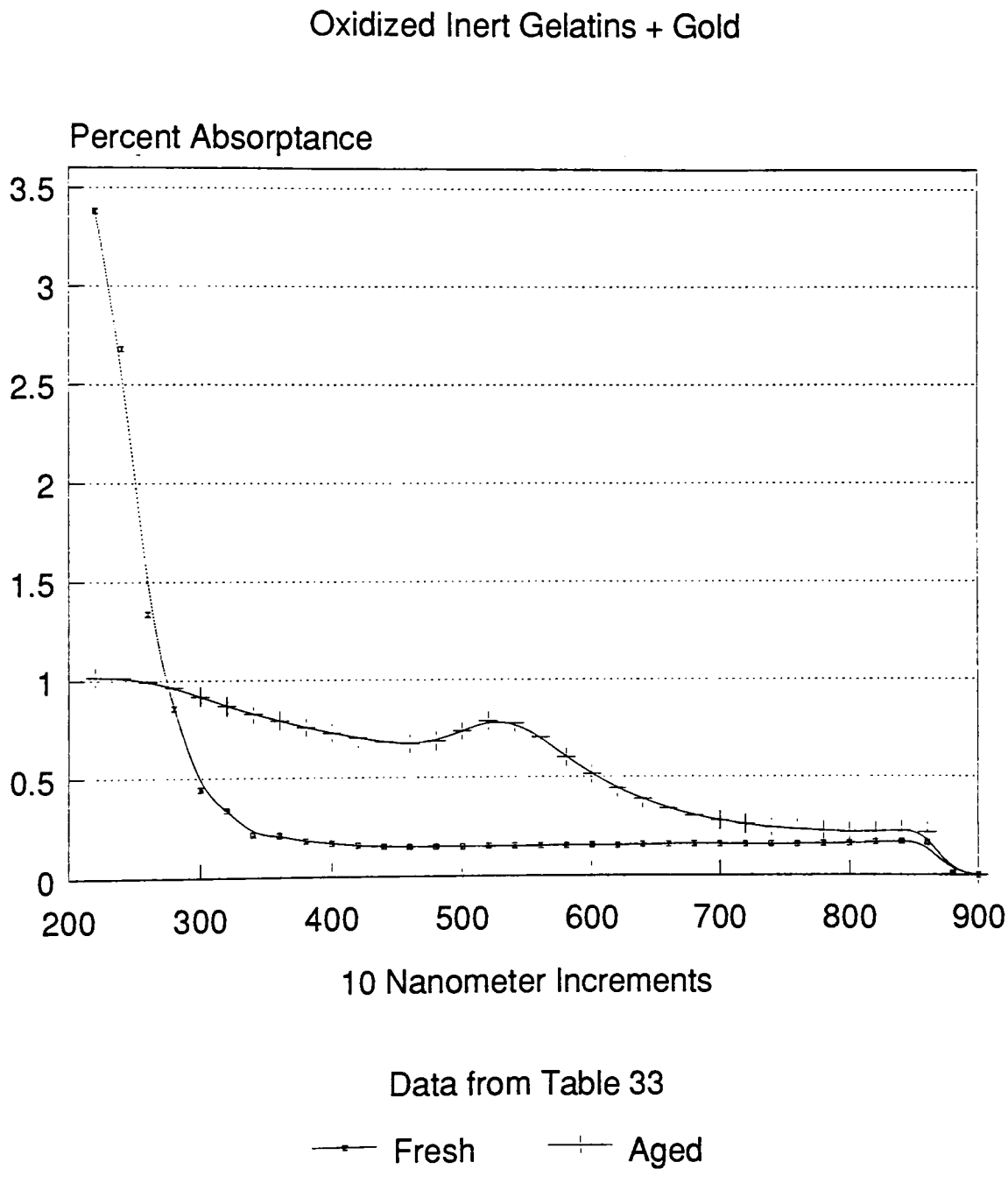

Oxidized Inert Gelatins + Gold
Percent Absorptance
3.5
3
2.5
2
1.5
1
0.5
0
200
300
400
500
600
700
800
900
10 Nanometer Increments
Data from Table 33
Fresh
Aged

Figure 18

Phthalated Gelatin + Gold

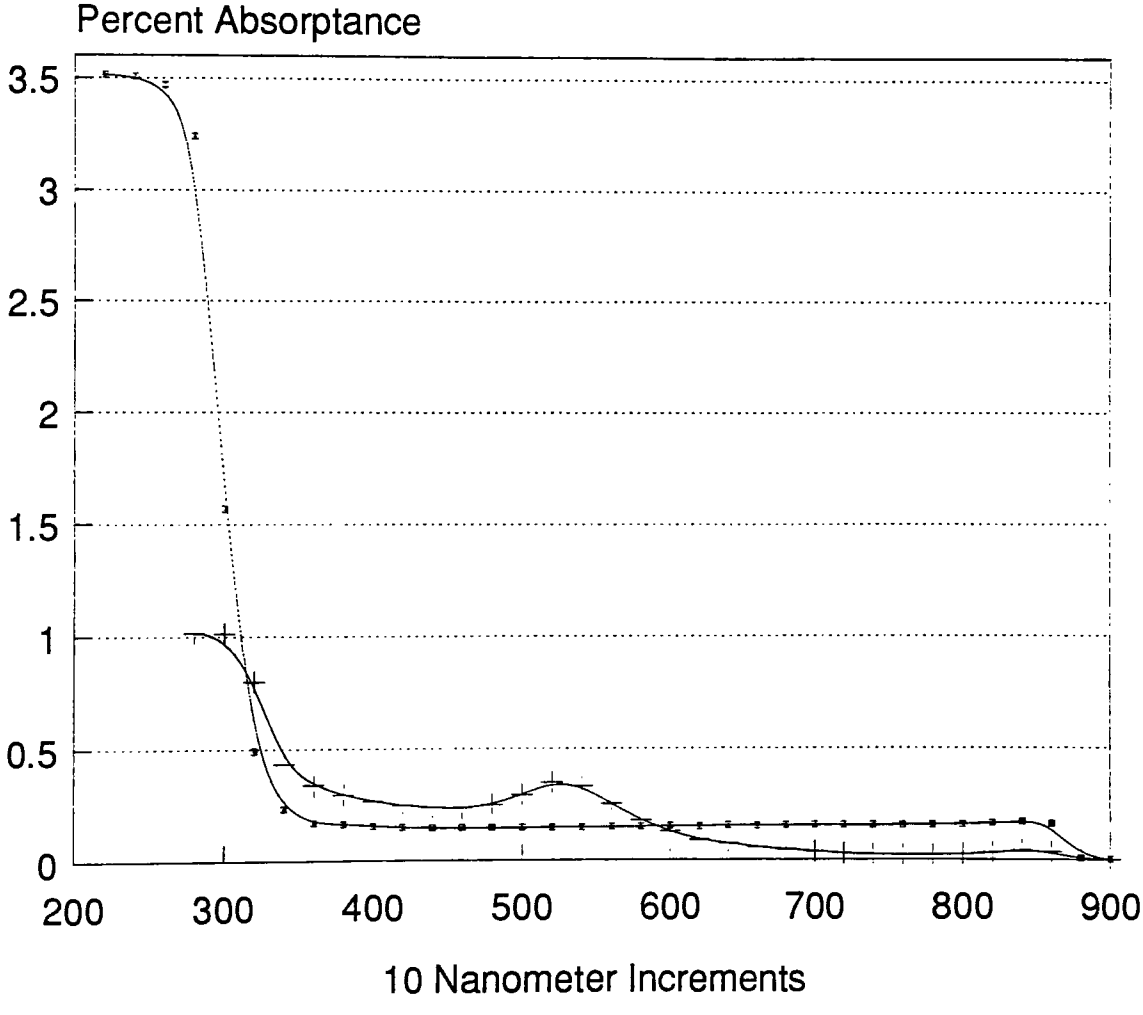


Figure 19

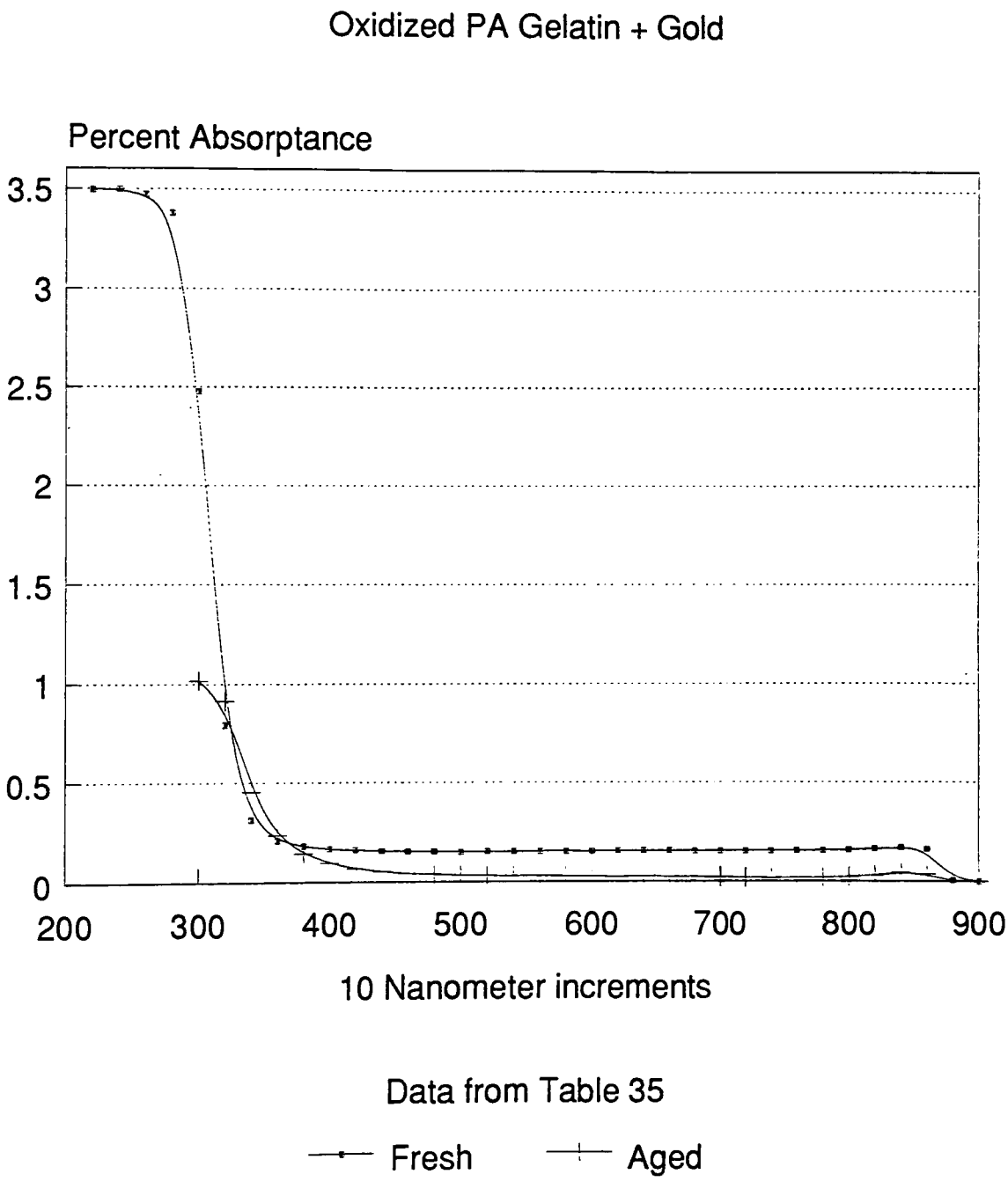

Oxidized PA Gelatin + Gold
Percent Absorptance
3.5
3
2.5
2
1.5
1
0.5
0
200
300
400
500
600
700
800
900
10 Nanometer increments
Data from Table 35
Fresh
Aged

Figure 20

Potassium Tetrachloroaurate

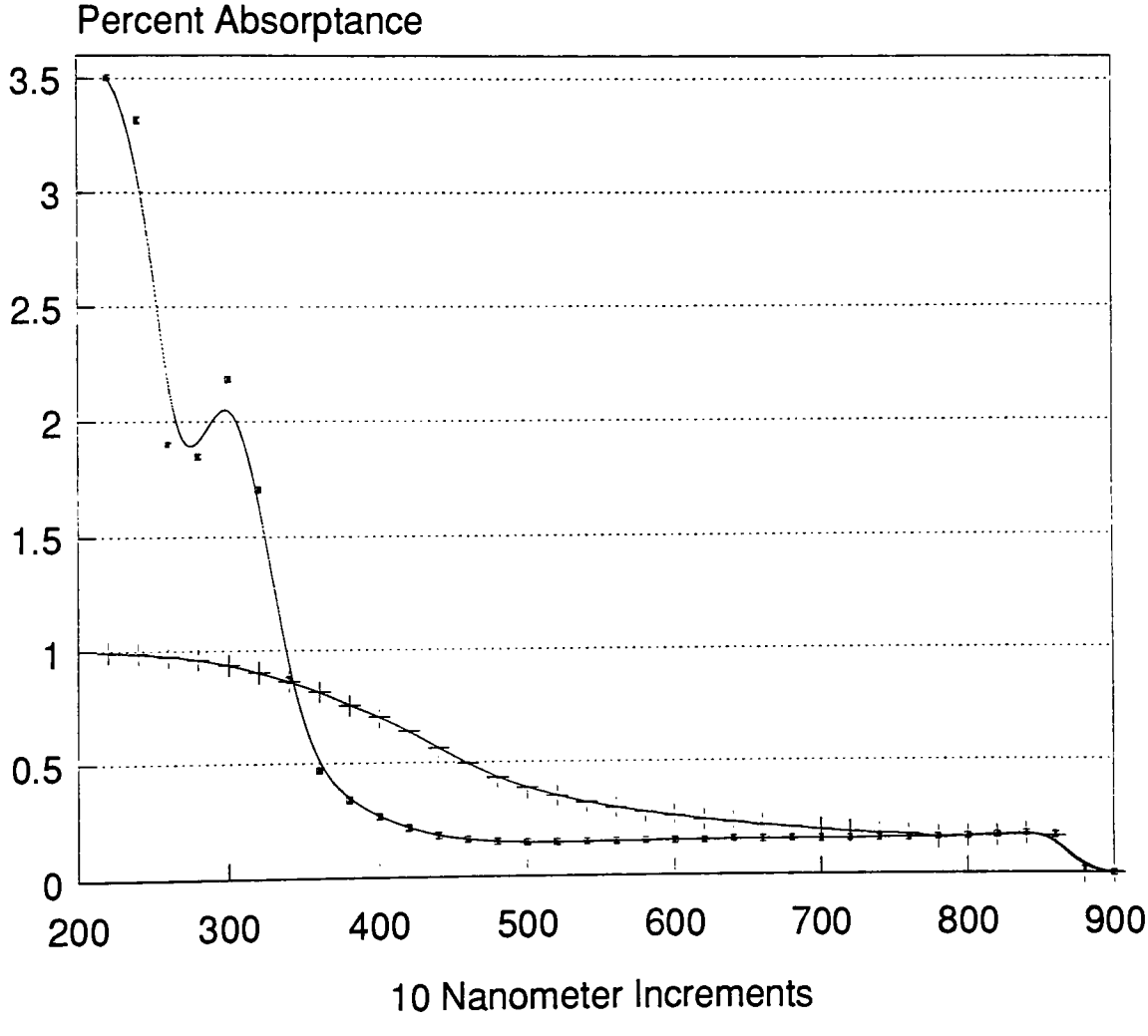


Table 28
Inert Gelatin 1.0%
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.173	-0.024
880	-0.165	-0.024
860	-0.012	0.039
840	-0.003	0.042
820	-0.008	0.033
800	-0.012	0.026
780	-0.014	0.024
760	-0.014	0.024
740	-0.014	0.024
720	-0.014	0.028
700	-0.013	0.032
680	-0.011	0.036
660	-0.010	0.040
640	-0.008	0.044
620	-0.010	0.044
600	-0.007	0.051
580	-0.005	0.054
560	-0.004	0.057
540	-0.002	0.059
520	0.001	0.061
500	0.003	0.064
480	0.010	0.079
460	0.016	0.083
440	0.026	0.097
420	0.037	0.116
400	0.053	0.134
380	0.074	0.161
360	0.110	0.207
340	0.169	0.273
320	0.242	0.338
300	0.345	0.431
280	0.602	0.654
260	0.975	0.820
240	2.265	0.991
220	3.175	1.000

Table 29
Oxidized Inert Gelatin 1.4%
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.178	-0.025
880	-0.170	-0.025
860	-0.017	0.021
840	-0.008	0.032
820	-0.014	0.020
800	-0.019	0.012
780	-0.021	0.010
760	-0.023	0.008
740	-0.024	0.008
720	-0.025	0.009
700	-0.025	0.008
680	-0.024	0.014
660	-0.025	0.015
640	-0.024	0.019
620	-0.028	0.013
600	-0.027	0.017
580	-0.028	0.018
560	-0.028	0.020
540	-0.030	0.018
520	-0.030	0.020
500	-0.032	0.021
480	-0.030	0.024
460	-0.030	0.028
440	-0.028	0.034
420	-0.025	0.044
400	-0.020	0.058
380	-0.009	0.079
360	0.015	0.122
340	0.077	0.201
320	0.148	0.289
300	0.226	0.408
280	0.694	0.739
260	1.108	0.868
240	2.527	0.997
220	3.179	1.000

Table 30
Phthalated Gelatin 1.0%
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	0.009	-0.018
880	0.007	-0.018
860	0.007	0.184
840	0.008	0.196
820	0.006	0.197
800	0.005	0.198
780	0.005	0.204
760	0.005	0.214
740	0.004	0.224
720	0.004	0.237
700	0.005	0.252
680	0.004	0.268
660	0.004	0.284
640	0.005	0.303
620	0.001	0.318
600	0.003	0.340
580	0.002	0.361
560	0.002	0.383
540	0.001	0.411
520	0.002	0.439
500	0.000	0.474
480	0.001	0.510
460	0.001	0.551
440	0.002	0.587
420	0.004	0.641
400	0.007	0.689
380	0.013	0.736
360	0.024	0.781
340	0.078	0.845
320	0.408	0.906
300	1.703	0.963
280	3.212	1.000
260	3.391	
240	3.428	
220	3.431	

Table 31
Oxidized Phthalated Gelatin 1.6%
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	0.015	-0.021
880	0.012	-0.021
860	0.013	0.030
840	0.013	0.041
820	0.012	0.034
800	0.011	0.021
780	0.012	0.019
760	0.012	0.014
740	0.013	0.015
720	0.014	0.017
700	0.014	0.020
680	0.015	0.021
660	0.015	0.022
640	0.017	0.030
620	0.012	0.023
600	0.014	0.031
580	0.014	0.032
560	0.015	0.037
540	0.014	0.038
520	0.016	0.041
500	0.015	0.044
480	0.018	0.051
460	0.021	0.058
440	0.025	0.069
420	0.031	0.085
400	0.041	0.112
380	0.059	0.152
360	0.095	0.225
340	0.237	0.454
320	0.947	0.921
300	2.947	1.000
280	3.357	
260	3.420	
240	3.442	
220	3.440	

Table 32
Inert Gelatin 1.0%
Plus 0.10% Gold
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.177	-0.016
880	-0.170	-0.016
860	-0.016	0.200
840	-0.008	0.208
820	-0.014	0.202
800	-0.018	0.201
780	-0.020	0.208
760	-0.022	0.216
740	-0.022	0.224
720	-0.023	0.241
700	-0.023	0.261
680	-0.022	0.285
660	-0.023	0.323
640	-0.022	0.372
620	-0.026	0.424
600	-0.025	0.499
580	-0.026	0.584
560	-0.026	0.688
540	-0.027	0.760
520	-0.027	0.773
500	-0.029	0.720
480	-0.028	0.670
460	-0.028	0.657
440	-0.027	0.666
420	-0.024	0.687
400	-0.018	0.713
380	-0.007	0.743
360	0.015	0.779
340	0.051	0.814
320	0.102	0.855
300	0.183	0.904
280	0.366	0.952
260	0.621	0.979
240	1.624	0.998
220	3.096	1.000

Table 33
Oxidized Inert Gelatin 1.4%
Plus 0.10% Gold
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.174	-0.018
880	-0.167	-0.018
860	-0.013	0.024
840	-0.005	0.034
820	-0.010	0.022
800	-0.014	0.016
780	-0.016	0.013
760	-0.017	0.010
740	-0.018	0.011
720	-0.017	0.012
700	-0.017	0.014
680	-0.016	0.017
660	-0.017	0.018
640	-0.017	0.021
620	-0.022	0.018
600	-0.020	0.023
580	-0.022	0.022
560	-0.022	0.024
540	-0.024	0.027
520	-0.024	0.030
500	-0.026	0.031
480	-0.025	0.037
460	-0.025	0.043
440	-0.022	0.052
420	-0.018	0.068
400	-0.010	0.085
380	0.005	0.132
360	0.035	0.202
340	0.094	0.309
320	0.163	0.428
300	0.267	0.601
280	0.683	0.873
260	1.164	0.953
240	2.504	1.000
220	3.205	

Table 34
Phthalated Gelatin 1.0%
Plus 0.10% Gold
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.176	-0.017
880	-0.169	-0.017
860	-0.015	0.016
840	-0.006	0.024
820	-0.012	0.015
800	-0.017	0.006
780	-0.019	0.004
760	-0.020	0.004
740	-0.021	0.006
720	-0.021	0.011
700	-0.021	0.019
680	-0.021	0.030
660	-0.022	0.040
640	-0.021	0.056
620	-0.025	0.073
600	-0.024	0.111
580	-0.026	0.161
560	-0.027	0.234
540	-0.028	0.312
520	-0.028	0.330
500	-0.030	0.276
480	-0.030	0.233
460	-0.030	0.217
440	-0.029	0.220
420	-0.026	0.231
400	-0.020	0.249
380	-0.011	0.278
360	0.006	0.321
340	0.057	0.417
320	0.316	0.782
300	1.394	0.996
280	3.066	1.000
260	3.293	
240	3.331	
220	3.338	

Table 35
Oxidized Phthalated Gelatin 1.6%
Plus 0.10% Gold
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.174	-0.017
880	-0.169	-0.017
860	-0.013	0.018
840	-0.004	0.026
820	-0.010	0.014
800	-0.014	0.005
780	-0.017	0.003
760	-0.018	0.001
740	-0.019	0.000
720	-0.019	0.002
700	-0.019	0.004
680	-0.019	0.007
660	-0.017	0.007
640	-0.018	0.011
620	-0.017	0.007
600	-0.021	0.010
580	-0.019	0.011
560	-0.020	0.013
540	-0.020	0.013
520	-0.021	0.015
500	-0.022	0.016
480	-0.021	0.021
460	-0.020	0.025
440	-0.017	0.036
420	-0.013	0.051
400	-0.006	0.079
380	0.007	0.128
360	0.038	0.221
340	0.143	0.438
320	0.619	0.896
300	2.303	1.000
280	3.204	
260	3.298	
240	3.323	
220	3.321	

Table 36
0.10% Gold
Spectra of December 8, 1988
and March 2, 1989

Wavelength (nanometers)	Percent Absorptances December	March
900	-0.184	-0.016
880	-0.170	-0.016
860	-0.018	0.144
840	-0.011	0.154
820	-0.017	0.149
800	-0.022	0.146
780	-0.025	0.140
760	-0.027	0.157
740	-0.027	0.160
720	-0.028	0.168
700	-0.029	0.178
680	-0.028	0.189
660	-0.029	0.199
640	-0.028	0.213
620	-0.033	0.224
600	-0.032	0.243
580	-0.033	0.259
560	-0.034	0.280
540	-0.036	0.303
520	-0.037	0.333
500	-0.037	0.368
480	-0.032	0.415
460	-0.022	0.477
440	-0.004	0.549
420	0.030	0.624
400	0.080	0.689
380	0.153	0.749
360	0.283	0.801
340	0.687	0.847
320	1.521	0.886
300	1.998	0.921
280	1.663	0.946
260	1.712	0.961
240	3.134	0.973
220	3.320	0.978

5.0 References

Babcock, T.A., Ferguson, P.M., Lewis, W.C., and James, T.H.,"Chemical Sensitization Using Hydrogen Gas, Part II. With Other Types of Chemical Sensitization," Photogr. Sci. Eng. v19: 211(1975).

Babcock, T.A., and James, T.H. "Use of Hydrogen Hypersensitization to Diminish Recombination and Produce Emulsion Coatings of High Quantum Efficiency," J. Photogr. Sci. v24: 19(1976).

Berriman, R.W., and Gilman, P.B. Jr., "Spectral Sensitization of Mobile Positive Holes," Photogr. Sci. Eng. v17: 235(1973).

Berry, C.R., "Electron and Hole Traps in AgBr," J. Photogr. Sci. v21: 202(1973).

Burge, G., "Gold-Containing Surface States on Photographic AgBr Grains: Roles besides Photoelectron-Trapping," J. Electrochem. Soc. v129: 591(1982).

Cash, D.J., "The Kinetics of Sulphur Sensitization: Sulphide Migration During Digestion," J. Photogr. Sci. v20: 223(1972).

Cash, D.J., "The Effect of Gold Salts on the Chemical Mechanisms of Photographic Sulfur Sensitization of Silver Halide Photoemulsions: Stabilization of Adsorbed Sulfide at the Crystal Surface," Photogr. Sci. Eng. v27: 156(1983).

Codling, A.B.J., "The Luminescence of Silver Bromide Emulsions at 77 K," Photogr. Sci. Eng. v19: 44(1975).

Collier, S.S., "Electron Trapping and Recombination in Core-Shell Emulsions at 77 K," Photogr. Sci. Eng. v20: 43(1976).

Collier, S.S., "Reduction Sensitization of a 1.08 micron AgBr Octahedral Emulsion," Photogr. Sci. Eng. v23: 113(1979).

Collier, S.S., "Speed and Fog Increases from the Addition of Surface Reduction Sensitization to a Surface Sulfur-Plus-Gold Sensitized 1 micron AgBr Octahedral Emulsion," Photogr. Sci. Eng. v26: 98(1982).

Deri, R.J., and Spoonhower, J.P., "Drift Mobility, Electron Trapping, and diffusion-limited kinetics in Sulfur-Sensitized AgBr microcrystals," JJ. Appl. Phys. v57: 2806(1985).

Evans, F.J., "Photographic Element Containing Monodispersed Unfogged Silver Halide Grains, Chemically Sensitized Internally and Externally," United States Patent 3,761,276 granted September 25, 1973.

Evans, F.J., and Gilman, P.B. Jr., "Comparison of the Spectral Sensitization of Surface and Internally Sensitized Core/Shell Octahedral Silver Bromide Emulsions", Photogr. Sci. Eng. v19: 333(1975).

Faelens, P., "Mechanism of the Elimination of High Intensity Reciprocity Law Failure by Gold-Sensitization", J. Photogr. Sci. v13: 54(1965).

Faelens, P., "About the Nature and the Role of the Sensitivity Speck Formed During Gold Ripening," J. Photogr. Sci. v26: 144(1978).

Farnell, G.C., and Solman, L.R., "The Role of Gold in Sulfur-Plus-Gold Sensitization," J. Photogr. Sci. v24: 203(1976).

Farnell, G.C., and Solman, L.R., "Further Comments on the Role of Gold in Sulfur-Plus-Gold Sensitization," J. Photogr. Sci. v28: 185(1980).

Galvin, J.P., "Properties of Holes in Silver Halides: A review," Photogr. Sci. Eng. v16: 69(1972).

Hailstone, R.K., Liebert, N.B., Levy, M., and Hamilton, J.F., "Latent Subimage in a AgBr Model Emulsion. 1. Sulfur-Plus-Gold-Sensitized Versions," J. Imag. Sci. v31: 185(1987).

Haist, G.M., "Modern Photographic Processing," John Wiley and Sons, New York, 1979.

Hamilton, J.F., and Baetzold, R.C., "The Paradox of Ag2 Centers on AgBr: Reduction Sensitization vs. Photolysis," Photogr. Sci. Eng. v25: 189(1981).

Hamilton, J.F., "Toward a Quantitative Latent-Image Theory," Photogr. Sci. Eng. v26: 263(1982).

Hamilton, J.F., "A Modified Proposal for the Mechanism of Sulfur Sensitization in Terms of Capture Cross Section," Photogr. Sci. Eng. v27: 225(1983).

Harbison, J.M., and Hamilton, J.F., "Function of Gold in Sulfur-Plus-Gold Sensitization," Photogr. Sci. Eng. v19: 322(1975).

Harbison, J.M., Private Communication, dated September 24, 1991.

Hewitson, E.H., and McClintock, T., "Process for Preparing Photographic Emulsions," United States Patent 2,618,556 granted November 18, 1952.

Illingsworth, B.D., "Sulfur Group Sensitized Emulsions," United States Patent 3,320,069 granted May 16, 1967.

James, T.H., "The Site of Reaction in Direct Photographic Development. II. Kinetics of Development Initiated by Gold Nuclei," J. Colloid Sci. v3: 447(1948).

James, T.H., Vaneslow, W., and Quirk, R.F., "Mechanism of Superadditivity in Photographic Development," Phot. Sci. Tech. v19B: 156(1953).

James, T.H., "The Theory of the Photographic Process, 4th Ed.," MacMillan and Co., New York, 1977.

Junkers, G., Klein, E., Moisar, E., "Topography of Latent Image Doping Centres in Silver Halide Microcrystals," J. Photogr. Sci. v22: 174(1974).

Kellogg, L.M., "The Effect of Sulfur and Sulfur-Plus-Gold Sensitizing Centers on the Photoelectron lifetimes and the Photographic Response in AgBr Emulsions," Papers from 28th Annual Conf. SPSE, May(1975), Denver, p. 212.

Leubner, I.H., Jagannathan, R., and Wey, J.S., "Formation of Silver Bromide Crystals in Double-Jet Precipitation," Photogr. Sci. Eng. v24: 268(1980).

Leubner, I.H., "Crystal Formation (Nucleation) Under Kinetically and Diffusion Controlled Growth Conditions," Paper presented at the 39th Annual Conf. SPSE, May(1986a), Minneapolis, and at the International Congress of Photographic Science, September(1986a), Cologne, FRG.

Leubner, I.H., "Crystal Formation (Nucleation) in the Presence of Ostwald Ripening Agents," Paper presented at the 39th Annual Conf. SPSE, May(1986b), Minneapolis, and at the International Congress of Photographic Science, September(1986b), Cologne, FRG.

Leubner, I.H., "Crystal Formation (Nucleation) in the Presence of Growth Restrainers," Paper presented at the 39th Annual Conf. SPSE, May(1986c), Minneapolis, and at the International Congress of Photographic Science, September(1986c), Cologne, FRG.

Locker, D.J., "Energies of Activation and the Kinetics of Fog Center and Sensitivity Center Formation During Chemical Sensitization," Photogr. Sci. Eng. v20: 242(1976).

Lowe, W.G., Jones, J.E., and Roberts, H.E., "Some Chemical Factors in Emulsion Sensitivity," Proc. Bristol Symposium, Bristol, U.K., 1950.

Marchetti, A.P., Collier, S.S., and Crews, N.P., "Surface Dependence of Sulfur, Gold, and Sulfur-Plus-Gold Sensitizations," Photogr. Sci. Eng. v28: 146(1984).

Maskasky, J., "An Enhanced Understanding of Silver Halide Tabular-Grain Growth," J. Imag. Sci. v31: 15(1987).

Moisar, E., "A Comparitive Study of Latent Image Formation," J. Photogr. Sci. v13: 46(1965).

Moisar, E., Granzer, F., Dautrich, D., and Palm, E., "Formation and Properties of Sub-Image and Latent-Image Silver Specks, Part I: Thermodynamics of Silver Speck Formation," J. Photogr. Sci. v25: 12(1977).

Moisar, E., "Formation, Nature, and Action of Sensitivity Centers and Latent Image Specks, Part I: Chemical Sensitization-A Review," Photogr. Sci. Eng. v25: 45(1981).

Moisar, E., and Granzer, F., "Formation, Nature, and Action of Sensitivity Centers and Latent Image Specks, Part II: Silver Nucleation, Fog, and the Relation Grain Size/Speed," Photogr. Sci. Eng. v26: 1(1982).

Moisar, E., "Thermodynamics and Kinetic Aspects of Silver Formation," Photogr. Sci. Eng. v26: 124(1982).

Mueller, F.W.H., "30 Years of Gold Sensitization," Photogr. Sci. Eng. v10: 338(1966).

Pitt, D.A., Rachu, M.L., and Sayhun, M.R.V. "Model for the Chemical Sensitization of Silver Halide Photographic Emulsions with Sulfur and Gold," Photogr. Sci. Eng. v25: 57(1981).

Pouradier, J., Gadet, M.C., et Chateau H., "Electrochimie des Sels D'Or II.-Acides auro et Aurichlorohydriques et Sels Correspondants," J. Chim. Phys. v62: 203(1965).

Sayhun, M.R.V., "Concerning the Contribution of Coprecipitated Sulfur Impurities to the Photographic Sensitivity of Silver Halide Emulsions," Photogr. Sci. Eng. v26: 163(1982).

Simson, J.M., and Gaugh, W.S., "Desensitization by Efficient Spectral Sensitizers," Photogr. Sci. Eng. v19: 339(1975).

Spencer, H.E., and Atwell, R.E., "Reduction-Plus-Sulfur Sensitization and Latent Image Formation in a Model AgBr Dispersion," J. Opt. Sci. Am. v58: 1131(1968).

Spencer, H.E., DeCann, C.A., and McCleary, R.T., "Gold Latensification: Replacement or Plating of Silver by Gold?," J. Imag. Sci. v31: 8(1987).

Sturmer, D.M., and Gaugh, W.S., "Spectral Sensitization and Calculated Energy Levels: Core/Shell Emulsions," Photogr. Sci. Eng. v19: 344(1975a).

Sturmer, D.M., and Blackburn, L.N., "Location of Sulfide and Photographic Sensitivity Sites in Internally Sulfur-Plus-Gold sensitized Core/Shell Grains ," Photogr. Sci. Eng. v19: 352(1975b).

Sutherns, E.A., "The Reliability of Bleaching Techniques for the Determination of Latent Image Distribution in Silver Bromide and Iodobromide Emulsions," J. Photogr. Sci. v9: 217(1961).

Tan, Y.T., and Marchetti, A.P., "The Mobility of Gold in Silver Chloride," J. Appl. Phys. v52: 3400(1981).

Tani, T., "Photographic Effects of Electron and Positive Hole Traps, I. Chemical Sensitization, Reducing Agents, and Phenosafranine," Photogr. Sci. Eng. v15: 28(1971a).

Tani, T., "Photographic Effects of Electron and Positive Hole Traps, II. Reduction Sensitization in Octahedral Silver Bromide Grains," Photogr. Sci. Eng. v15: 181(1971b).

Tani, T., "Photographic Effects of Electron and Positive Hole Traps, IV. Reduction Sensitization in Various Silver Bromide Grains," Photogr. Sci. Eng. v16: 35(1972).

Tani, T., "Photographic Effects of Electron and Positive Hole Traps in Silver Halides VII: Interaction between Reduction Sensitization and Desensitization by Dyes on Various Silver Bromide Grains," Photogr. Sci. Eng. v18: 569(1974).

Tani, T., "Photographic Effects of Electron and Positive Hole Traps in Silver Halides IX: Factors Influencing Desensitization Caused by Sensitizing and Desensitizing Dyes," Photogr. Sci. Eng. v18: 576(1974).

Tani, T., "A Study of the Properties of Clusters of Photographic Interest by Means of a Redox Buffer Solution," Photogr. Sci. Eng. v27: 75(1983).

Wey, J.S., and Strong, R.W., "Influence of the Gibbs-Thomson Effect on the Growth Behavior of AgBr Crystals," Photogr. Sci. Eng. v21: 248(1977).

Whitenack, S.K., "Comparison of Sulfur and Gold Sensitizations of an Octahedral Silver Bromide Emulsion, Senior Thesis," The Center for Imaging Science of the Rochester Institute of Technology, May, 1988.

Yutzy, H.C., and Russell, F.J., "Method of Preparing Photographic Emulsions," United States Patent 2,614,929 granted October 21, 1952.

Zuleta, J.A., and Friedman, P., "Emulsion 1, A Routine for Controlling Growth in Double Jet Precipitations," Unpublished work, The Center for Imaging Science of the Rochester Institute of Technology, 1987.